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A NEW
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A CHEMICAL PHILOSOPHY.

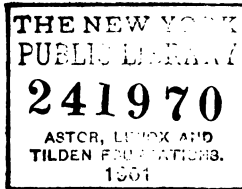
BY

THOMAS STERRY HUNT, M.A., LL.D. (CANTAB.),
AUTHOR OF "CHEMICAL AND GEOLOGICAL ESSAYS," "MINERAL
PHYSIOLOGY AND PHYSIOGRAPHY,"
ETC., ETC.

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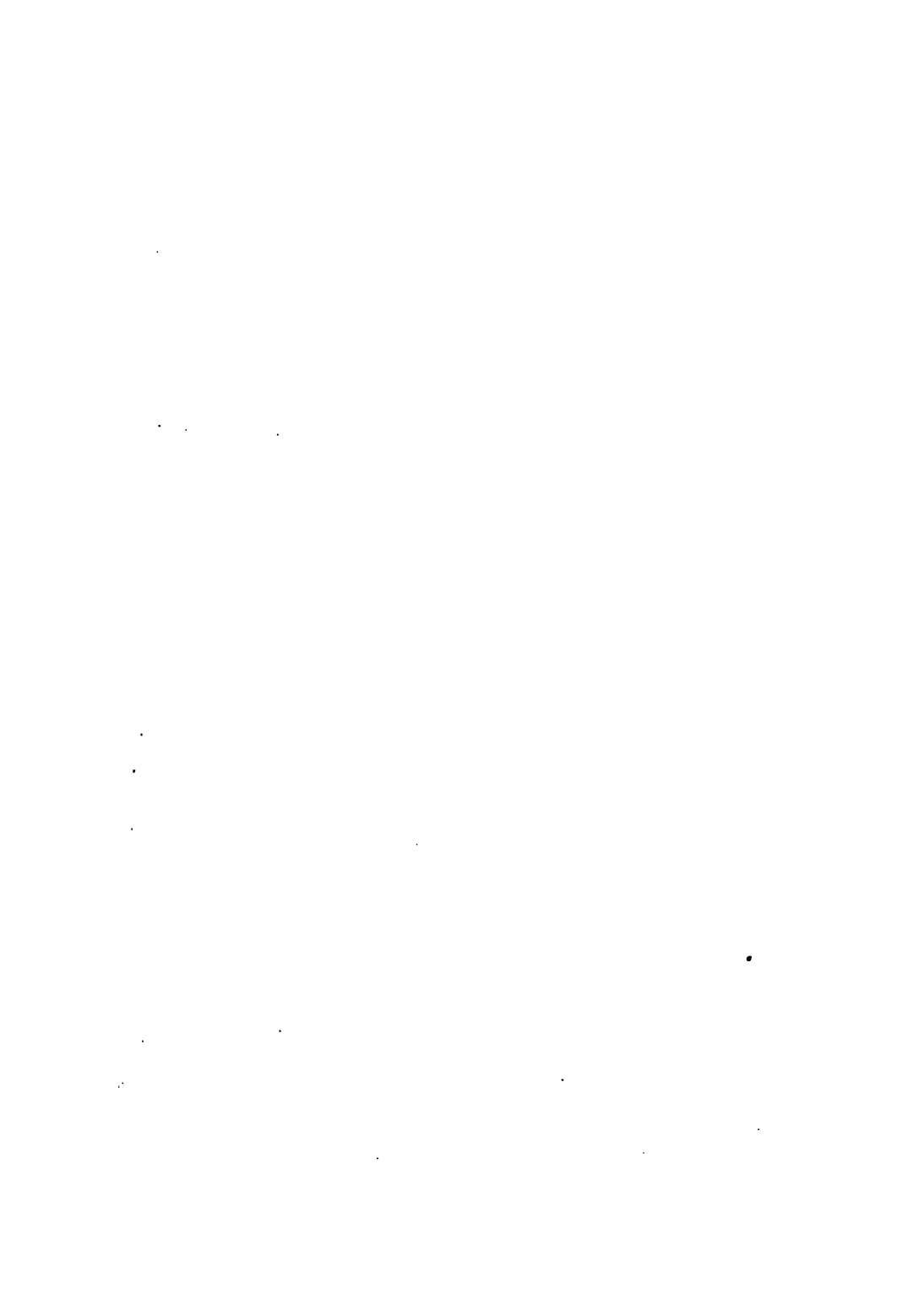
TO

J. B. STALLO,
CITIZEN—JURIST—PHILOSOPHER,

THIS VOLUME IS GRATEFULLY

DEDICATED BY THE

AUTHOR.



PREFACE.

It is now more than thirty-eight years since the author, repelled by the contradictions which result from the introduction into chemistry of the atomic hypothesis, and seeking a better foundation than that on which Dalton endeavored to build a theory of the science, began a series of publications, having for their object, in the words employed in 1853, to define the "principles which may serve as the basis of a sound theory of chemistry," and at the same time "to enlarge and simplify the plan of chemical science." In pursuance of this plan to the present time, he has persistently followed the line of argument foreshadowed in 1848, and fully stated in 1853. Advances were made in the succeeding years; but the crucial problem, the solution of which was required to complete the projected philosophy of chemistry, namely, that of the relation of equivalent weight to

specific gravity in liquids and solids, remained unresolved until the summer of 1886. With its solution, the author believes that the object so long ago proposed has been attained, and that we have the elements of a new and simple Chemical Philosophy, which he ventures to designate A New Basis for Chemistry.

Rejecting all hypotheses regarding the constitution of matter, as irrelevant to the study of chemistry when rightly understood, and as pertaining to the wholly distinct realm of dynamics, the author has attempted to define the limit between the two, and to show that the phenomena of solution, fusion, volatilization, liquefaction, solidification, and crystallization, — in a word, all changes of state, — belong to the domain of chemistry, and that, from a right consideration of these, some of the most obscure problems of the science become clear. He has therefore endeavored, in a series of chapters, and, in large part, in language quoted from his earlier writings, to define the principles upon which he believes may one day be built a New Chemistry.

The reader will note that the plan and the

limits of this little volume exclude the discussion of many subjects which would find a place in a systematic treatise on chemical theory. Among these are the consideration of the periodic law in relation to the law of numbers, the question of valency, and the problems of thermo-chemistry, all of which must be reserved for another time and place.

It would be unjust on the part of the author not to express his many obligations to J. B. Stallo, now the American Minister at the Court of Italy, whose suggestive volume on the Philosophy of Nature, in 1848, was, at that early date, a source of inspiration; whose friendship during many years has encouraged the writer in his labors; and whose later volume, on The Concepts and Theories of Modern Physics, in 1882, has served to confirm him in the position which he has long maintained with regard to the philosophy of the sciences. To Stallo, therefore, this book is dedicated.

BOSTON, January 1, 1887.

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A BASIS FOR CHEMISTRY.

CHAPTER I.

INTRODUCTION.

§ 1. At an early period in his chemical studies, the writer was led to adopt certain principles which, as said in 1853, would, it was thought, "be found to enlarge and simplify the plan of chemical science," and might "serve as the basis of a sound theory, of chemistry," which he believed to be wanting. His principal publications on this subject, from 1848 to 1886, seventeen in number, are as follows:—

1. ON SOME ANOMALIES IN THE ATOMIC VOLUMES OF SULPHUR AND NITROGEN, WITH REMARKS ON CHEMICAL CLASSIFICATION; American Journal of Science for September, 1848 (vi. 170-178).

2. ON SOME PRINCIPLES TO BE CONSIDERED IN CHEMICAL CLASSIFICATION; read at the first

meeting of the American Association for the Advancement of Science, Philadelphia, September, 1848, and published in the American Journal of Science in 1849 (vol. vii. 399-405; viii. 89-95).

3. A short treatise on ORGANIC CHEMISTRY, forming Part IV. (pp. 377-538) of the First Principles of Chemistry by B. Silliman, Jr., third edition, 1852. The novel points in chemical theory in this treatise are resumed by the writer in the American Journal of Science for 1853 (vol. xv. 150-152), and set forth more at length in the next paper mentioned.

4. ON THE THEORY OF CHEMICAL CHANGES AND ON EQUIVALENT VOLUMES; published in March, 1853, in the American Journal of Science (xv. 226-234), reprinted in the same year in the London, Edinburgh, and Dublin Philosophical Magazine, and in a German translation in the Chemisches Centralblatt (1853, page 849).

5. ON THE CONSTITUTION AND EQUIVALENT VOLUME OF SOME MINERAL SPECIES; in the American Journal of Science for September, 1853 (xvi. 203-218).

6. ILLUSTRATIONS OF CHEMICAL HOMOLOGY; read before the American Association for the Advancement of Science, at Washington, May, 1854; published in its Transactions for that year (pages 237-247), and in part in the last named journal for September, 1854 (xviii. 269-271).

7. THOUGHTS ON SOLUTION AND THE CHEMICAL PROCESS; in the American Journal of Science for January, 1855 (xix. 100-103), and in the Chemical Gazette for the same year, page 90.

8. THE THEORY OF TYPES IN CHEMISTRY; in the American Journal of Science for March, 1861 (xxxi. 256-264).

9. SUR LA NATURE DU JADE; in the *Compte Rendu* of the French Academy of Sciences of June 29, 1863, and in an English translation by the author in the American Journal of Science for the same year (xxxvi. 426-428).

10. THE OBJECT AND METHOD OF MINERALOGY; read before the American Academy of Sciences in Boston, January, 1867, and published in the American Journal of Science for May of that year (xliii. 203-206).

11. THE CHEMISTRY OF THE PRIMEVAL EARTH; a lecture before the Royal Institution of Great Britain, London, May 31, 1867, published in the Proceedings of the Institution, and the Chemical News of June 21, 1867, several times reprinted, and translated into French in *Les Mondes*.

12. A CENTURY'S PROGRESS IN THEORETICAL CHEMISTRY; being an address delivered at the grave of Priestley, in Northumberland, Pennsylvania, on the Centennial of Chemistry, July 31, 1874, and published in the *American Chemist* for August and September of that year.

13. THE CHEMICAL AND GEOLOGICAL RELATIONS OF THE ATMOSPHERE; published in the *American Journal of Science* for May, 1880 (xix. 349-363).

14. THE DOMAIN OF PHYSIOLOGY; OR NATURE IN THOUGHT AND LANGUAGE; read before the National Academy of Sciences, Washington, April 18, 1881, and published in the *London, Edinburgh, and Dublin Philosophical Magazine* for October of that year (V. xii. 223-253).

15. CELESTIAL CHEMISTRY FROM THE TIME

OF NEWTON; read before the Philosophical Society of Cambridge, England, Nov. 28, 1881, and published in its Proceedings (vol. IV. part iii); in the Chemical News, and in the American Journal of Science for February, 1882 (xxiii. 123-133).

16. A NATURAL SYSTEM IN MINERALOGY, WITH A CLASSIFICATION OF SILICATES; read before the National Academy of Sciences, at Washington, in April, 1885, and before the Royal Society of Canada, at Ottawa, in May, 1885, and published in the Transactions of the latter Society for the same year (vol. III. part iii. pp. 25-93).

17. THE LAW OF VOLUMES IN CHEMISTRY; published in Science for September 10, 1886.

Of the above papers, 4, 7, 8, 10, and 11, with portions of 5, 6, and 9, were reprinted in the author's Chemical and Geological Essays (first and second editions), in 1874 and 1878; while 13, 14, 15, and 16 appear, with some additions, in his Mineral Physiology and Physiography, in 1886. A general view of all these was embodied in two papers, entitled: A BASIS FOR CHEMISTRY; and HARDNESS AND CHEMICAL

INDIFFERENCE IN SOLIDS;—read before the National Academy of Sciences, in Boston, November 9 and 11, and noticed in Science for November 19, 1886.

§ 2. The fundamental points in the author's system were already set forth in the earlier papers, prior to 1855; since which time great advances have been made in dynamical and chemical knowledge. The results of all these lead the writer to conclude that the principles laid down by him a generation since should be again brought forward, and presented in a concise form to the attention of the scientific public, with such additions as are required to complete the philosophy of chemistry then first enunciated.

The propositions which were advanced in the various publications named are here set forth, in large part in language quoted from these, in a series of chapters. In making such quotations, reference is made by appended numbers corresponding to those prefixed in the preceding list.

CHAPTER II.

NATURE OF THE CHEMICAL PROCESS.

§ 3. IN inquiring into the philosophy of chemistry, it was said in 1853: "We commence by distinguishing between those phenomena which belong to the domain of physics and those which belong to the chemical history of matter. Under the first head we have, besides the gravity of matter in the abstract, its various conditions of consistence, shape, and volume, with the relation of the latter to weight, constituting specific gravity, and the relations of heat, light, electricity, and magnetism." These not only "modify physically the specific characters of matter, but they have besides important relations to those higher processes which give rise to new species by a complete change in the specific phenomena of bodies. In the capacity of such changes consists the chemical activity of matter." Proceeding, then, to discuss the question of the

origin of new species, and the relations of individuals, it was said: "That mode of generation which produces individuals like the parent can present no analogy to the phenomena under consideration; *metagenesis* or alternate generation, and *metamorphosis*, are, however, to a certain extent, prefigured in the chemical changes of bodies." These terms were then adopted in chemical language; and it was said that *metagenesis*, or the production of new species where two or more are concerned, "is effected in two ways: by condensation and union on the one hand, and by expansion and division on the other. In the first case, two or more species unite and merge their specific character in those of a new species; in the second case, the process is reversed, and a body breaks up into two or more new species." Of chemical *metamorphosis*, which embraces the phenomena of polymerism, it was said: "In *metamorphosis* by condensation only one species is concerned; and in *metamorphosis* by expansion the result is homogeneous and without specific difference."

§ 4. "The chemical history of bodies is a record of these changes; it is, in fact, their

genealogy. . . . By union we rise to indefinitely higher species ; but in division a limit is reached in the production of species which seem incapable of farther division ; and these, being regarded as primary or original species, are called chemical elements." The processes of union and division " continually alternate with each other ; and a species produced by the first may yield by division species unlike its parents. From this succession results double decomposition, or equivalent substitution, which always involves a union followed by division ; although, under the ordinary conditions, the process cannot be arrested at the intermediate stage. In the production of hydrochloric gas from chlorine and hydrogen, union takes place, followed by immediate expansion without specific difference (metamorphosis) " ; while in the case of compounds of chlorine with hydrocarbons, which, under changed conditions, break up into hydrochloric acid and a chlorinized species, it was said, " we observe the intermediate stage."

" A body may divide into two or more new species ; yet it is evident that these did not pre-

exist in it, from the fact that a different division may yield other species whose pre-existence is incompatible with the last; nor can the pre-existence of any species but those which we have called primary be admitted as possible. . . . For these reasons it is conceived that the notion of pre-existing elements, or groups of elements, should find no place in the theory of chemistry. Of the relation which subsists between the higher species and those derived from them, we can only assert the possibility, and, under proper conditions, the certainty of producing the one from the other. Ultimate chemical analyses and the formulas deduced from them serve to show what changes are possible in any body, or to what new species it may give rise by its changes." (4.)

§ 5. The question of metamorphosis by condensation, or polymerism, noticed above, had already been discussed at some length in 1848, in considering the vapor-density of sulphur, when it was shown that, if regarded as "consisting of three equivalents combined in one, the density of its vapor is no longer an anomaly, as the sulphur-vapor is condensed to one-

third its normal bulk, and its equivalent number is $16 \times 3 = 48$ " [$32 \times 3 = 96$, in the present notation]. It was at the same time proposed to consider ozone as a similar triple group (OOO) corresponding to sulphur-vapor (SSS) and to (SOO). (1.) *Post*, § 56.

In the same year these conclusions were referred to in connection with polymerism in hydrocarbonaceous bodies, and allotropism in elements was explained as polymerism connected with a change in chemical relations. It was said : "Those substances which are considered as elementary may change their equivalents, at the same time undergoing a change in their densities; and, as we obtain from the ordinary equivalent and density an idea of 'the volume of the atom,' we say of those forms having an increased density and a corresponding increase of equivalent (so that the atomic volume remains unchanged) that two or more molecules have united in one. This is illustrated in the case of sulphur," and, as was farther shown, in the compounds of mercury, copper, and iron.

"The so-called elements may then possess

different atomic weights, which enjoy a simple relation to each other, and in these different states exhibit very different characters. When we speak of one of these as containing two or three atoms of another form condensed into one, it is only an expression in accordance with previously existing ideas. We can no longer attach to the atomic weights of the supposed elements an absolute value [that is, as being the weight of an absolutely elemental species]; and thus one of the characteristics which serve to distinguish them from known compounds is rendered of no importance." In farther illustration of this conception, it was then and there suggested that charcoal, graphite, and diamond being "polymeric modifications of elemental carbon," the first of these "is a species of anhydrid derived from cellulose"; and, moreover, that the allotropic red phosphorus might be a similar polymer;—a question which, it was said, "would be solved by a determination of its density in that state." (2.)

§ 6. In 1854, returning to the subject of chemical change, and discussing the question of double decomposition, it was illustrated by

the production of arsenious oxyd and chlorhydric acid by the action of water on terchlorid of arsenic, when it was said: "This decomposition of the solution of chlorid of arsenic is an example of what is generally called double elective affinity (*attractio electiva duplex*), and is generally explained by saying that the attraction of arsenic for oxygen, and that of chlorine for hydrogen, enable the chlorid and the water to decompose each other. But these elemental species do not exist in the solution, although they are possible results of its decomposition; and to explain the process in this manner is to ascribe it to the affinities of yet unformed species."

It was farther said that "double decomposition always involves union followed by division; although we cannot in every case arrest the process at its first stage. Under some changed conditions of temperature and pressure the decomposition may be counterpart of the previous union"; as in the example then given of mercury and oxygen. "When the division takes place in a sense different from the union, giving rise to new species, we have double decomposi-

tion. . . . It is only when looked upon as a momentary combination, followed by a decomposition, that the theory of double decomposition becomes intelligible and is in accordance with known facts. From the narrow limits of temperature which often include the processes, and from the ease with which light, warmth, friction, and pressure excite the decomposition of such bodies as the chlorid of nitrogen, the nitrite of ammonia, the oxyds of chlorine, and the metallic fulminates, we may conclude that within still narrower limits, and under conditions as yet undefined, many bodies may exhibit affinities for each other which are reversed by a very slight change of condition. In this way we may explain many of those obscure phenomena hitherto ascribed to *action by presence* or *catalysis*." (7.)

§ 7. The above doctrines were restated in 1861, as follows: "All chemical changes are reducible to union (identification) and division (differentiation). When in these changes only one species is concerned, we designate the process as metamorphosis, which is either by condensation or by expansion (homogeneous dif-

ferentiation). In metagenesis, on the contrary, unlike species may unite and, by a subsequent heterogeneous differentiation, give rise to new species, constituting what is called double decomposition; the results of which, differently interpreted, have given rise to the hypothesis of radicles, and the notion of substitution by residues, to express the relations between the parent bodies and their progeny. The chemical history of bodies is a record of these changes; it is, in fact, their genealogy, and in making use of typical formulas to indicate the derivation of chemical species, we should endeavor to show the ordinary modes of generation." (8.)

§ 8. In farther exposition of the nature of the chemical process, it was said in 1853: "Chemical species are homogeneous; *tota in minimis existit natura*." "Chemical combination is not a putting together of molecules, but an interpenetration of masses." "Chemical union is interpenetration, as taught by Kant, and not juxtaposition, as conceived by the atomistic chemists. When bodies unite, their bulks, like their specific characters, are lost in those of

the new species." (4.) In the year 1855 it was farther said of Kant's definition, that "the conception is mechanical, and therefore fails to give an adequate idea. The definition of Hegel, that *the chemical process is an identification of the different and a differentiation of the identical*, is, however, completely adequate. Chemical union involves an identification not only of the volumes (interpenetration mechanically considered), but of the specific character of the combining bodies, which are lost in those of the new species." (7.) In farther illustration of the above conception, in 1867, in referring to the speculations of Macvicar and Gaudin, as to "the architecture of crystalline molecules," it was written: "Nature builds up her units by interpenetration and identification, and not by juxtaposition of the chemical elements." (10.)

§ 9. In 1874, in again discussing this question, it was said: "In chemical change the uniting bodies come to occupy the same space at the same time, and the impenetrability of matter is seen to be no longer a fact. The volume of the combining substances is con-

founded, and all the physical and physiological characters which are our guides in the region of physics fail us, gravity alone excepted. The diamond dissolves in oxygen, and the identities of chlorine and sodium are lost in that of sea-salt. To say that chemical union is, in its essence, identification, as Hegel has defined it, seems to me the simplest statement conceivable. The type of the chemical process is found in solution, from which it is possible, under changed physical conditions, to regenerate the original species." (12.)

§ 10. Chemical change, then, may be defined as an integration or a disintegration of chemical species, resulting in the genesis of new species, which are themselves chemical; that is to say, mineral, and not organic. All of these "may be supposed to be formed from a single element, or *materia prima*, by the chemical process." "The chemical species, until it attains to individuality in the crystal, is essentially quantitative." (10.) Gases, liquids, and colloids have a specific existence, but no individuality; mechanical subdivision does not

destroy them. "The activities of the crystal are purely dynamic, and its crystalline individuality must be destroyed before it can be the subject of chemism, while the plant and the animal exhibit not only dynamical and chemical, but organogenic activities, which last are designated as vital phenomena." All of these are necessary for the preservation of the organism. The study of these vital activities constitutes a third division of physics, which we have elsewhere called biotics.

"Mineralogy is the science of inorganic matter, and studies its dynamical and chemical relations; while biology, which is the science of organic matter, adds to these the study of biotical relations. The dynamical and chemical activities which, in the mineral kingdom, give rise to the crystalline individual, are therein in static equilibrium. The organic individual, on the contrary, is kinetic, and maintains its equilibrium by perpetual adjustment with the outer world." "The physiology of matter in the abstract is dynamical; that of mineral forms is both dynamical and chemical; while that of organic

forms is at once dynamical, chemical, and biotical." (14.)¹

§ 11. By keeping in mind the above definitions, we shall avoid the error of modern students, who are disposed to confound dynamic activities with chemism itself, and thus to lose sight of the essential nature of the chemical process, which, as was pointed out in 1853 (§ 3), is to be clearly distinguished from

¹ These relations will be made more apparent by the help of a tabular view of the classification of the natural sciences from the writer's Mineral Physiology and Physiography, page 29.

NATURAL SCIENCES.	INORGANIC NATURE.	ORGANIC NATURE.
DESCRIPTIVE. —	MINERAL PHYSIOGRAPHY. —	BIOPHYSIOGRAPHY. —
General Physiography or Natural History.	Descriptive and Systematic Mineralogy; Geognosy; Geography; Descriptive Astronomy.	Organography; Descriptive and Systematic Botany and Zoölogy.
PHILOSOPHICAL. —	MINERAL PHYSIOLOGY. —	BIOPHYSIOLOGY. —
General Physiology or Natural Philosophy.	<i>Dynamics or Physics;</i> <i>Chemistry.</i> Geogeny; Theoretical Astronomy.	<i>Biotics.</i> Organogeny; Morphology; Physiological Botany and Zoölogy.

the phenomena belonging to what we may call dynamism. As examples of this prevailing confusion, it was said, in 1881: "Clifford wrote of molecular motion, 'which makes itself known as light, or radiant energy, or chemical action'; while Faraday was wont 'to express his conviction that the forces termed chemical affinity and electricity are one and the same.' " Helmholtz, from whom I here quote, adds: 'I think the facts leave no doubt that the very mightiest among the chemical forces are of electrical origin . . . but I do not suppose that other molecular forces are excluded, working directly from atom to atom.' " Similar language might be quoted from other not less eminent authorities, to show the vague notions still reigning in the minds of modern students as to the scope of chemistry, and its relation to dynamics.

"The activities which appear in dynamical and in chemical phenomena are one in essence, for force is one. The same is true of the activities manifested in organic growth, and even in thought; but the unity and mutual convertibility of different manifestations of force afford no ground for confounding, as some would do,

dynamics with chemism, or with vital or mental processes. All these phenomena are but evidences of universal animation; or, in other words, of an energy which is inherent in matter, the manifestations of which, as matter rises to higher stages of development, become more complex, as organic individuals are themselves more complex than mineral forms."

"When the energy which is in matter is manifested without reference to species, we call it simply dynamics; when it results in the production of mineral species, we call it chemics, or chemism; and when it gives rise to organisms, which may be defined as kinetic individuals, we distinguish it as vital, or biotic. In matter we must recognize, with Tyndall, 'the promise and the potency of all terrestrial life.'" (14.) Those dynamic activities which manifest themselves as electricity, temperature, and radiant energy, while attendant upon chemical processes, are yet to be as carefully distinguished from the essential phenomena of chemism as the latter are from those of biotics.

§ 12. In farther illustration of the nature of chemical combination, it was said, in 1853:

"Solution is a result of that tendency in nature which constantly leads to unity, condensation, identification." "Solution is chemical union, as is indicated by the attendant condensation." (4.) Again, in 1855, it was written: "All chemical union is nothing else than solution; the uniting species are, as it were, dissolved in each other; for solution is mutual." "Solution, then, being identification, the discussion as to whether metallic chlorids are changed into hydrochlorates when dissolved in water is meaningless. Such a solution is a unity, in which we can no more assert the existence of the chlorid, or of water, than of chlorine, hydrochloric acid, or a metallic oxyd; although these, and many others, are conceivable results of its differentiation." (7.) In the words already cited, — "The type of the chemical process is found in solution, from which it is possible, under changed physical conditions, to regenerate the original species." (12.)

CHAPTER III.

GENESIS OF THE CHEMICAL ELEMENTS.

§ 13. THERE remains to be considered another aspect of the chemical process — namely, the production, from a primal undifferentiated matter, of the chemical elements, as suggested by Lorenz Oken.¹ “The successive steps in

¹ In this connection we quote from page 3 of Tulk's Translation of Oken's Physiophilosophy, published by the Ray Society in 1847, with a preface by Oken himself, the following passage: “Physiophilosophy is divisible, therefore, into three parts. . . . The first division is the doctrine of the Whole (*de Toto*) — Mathesis. The second that of Singulars (*de Entibus*) — Ontology. The third that of the Whole in Singulars (*de Toto in Entibus*) — Biology. The science of the Whole must divide itself into two doctrines; into that of immaterial totalities — Pneumatogeny; and that of material totalities — Hylogeny. Ontology teaches us the phenomena of matter. The first phenomena of this are the heavenly bodies, comprehended by Cosmogony. These develop themselves further, and divide [differentiate] into the elements — Stoichiogeny. From these the earth-element develops itself still further, and divides into minerals — Mineralogy. These minerals unite in one collective body, and this is Geogeny. The Whole in Singulars is the living or Organic, which again divides into plants and animals.” The study of these includes Biology, with its subdivisions.

the ontological process are, first, Cosmogony, or the fashioning of the heavenly bodies from the previously formed matter; followed by the genesis therefrom of the chemical elements, Stoichiogeny." (14.)

§ 14. The conception of the genesis of the so-called chemical elements first took a definite form from the study of the equivalent weights of related elements, and from the law of numbers made apparent in hydrocarbonaceous bodies. Of this we wrote as follows, in 1874, in the essay on *A Century's Progress in Theoretical Chemistry* (12):—

"As early as 1829, Dobereiner called attention to the triads of related bodies, such as the groups of lithium, sodium, and potassium, and of calcium, strontium, and barium, in which the equivalent weight of the middle term is the mean of that of the extremes. Almost simultaneously, and apparently independently, Pettenkofer and Dumas took up again the question, in 1851, and noticed the fact that the numerical relations between these and many other mineral radicles are similar to those between the organic radicles known to

result from the condensation of successive equivalents of carbon and hydrogen, such as the olefines, the paraffines, and the alcohol radicles. The possibility that the mineral radicles, related alike in chemical characters and in equivalent weights, might, also, be composite bodies, was suggested by Dumas in 1857; and with this in view he undertook a re-examination of the equivalent weights of the elements. If, as the numbers adopted by Berzelius seemed to show, no simple ratios existed between those of related elements, the suggestion of Dumas was inadmissible; but if, on the contrary, as supposed by Prout, a simple and exact relation of this kind was established, it was not impossible that the view of their compound nature might be true."

"The results of many years of patient labor devoted to a re-examination of the equivalent weights of a great number of bodies, were given to the world by Dumas, in 1859; and from these he concluded that the law of Prout is so far true that the equivalent weights of the elements are multiples of a unity which is one-fourth that of hydrogen. . . . These re-

sults, and the analogies between the elements of mineral and of organic chemistry, both in chemical relations and in equivalent weights (which in the mean time had been carefully investigated and developed by J. P. Cooke), now led Dumas to reaffirm his conjecture that the mineral radicles may really be compounds, though their decomposition is perhaps beyond the possibilities of our chemical analysis." (12.)

§ 15. The next step in the development of the doctrine of Stoichiogeny, so far as known to the writer, is to be found in his lecture of 1867 (11), quoted below. The history thereof, and of certain views enunciated almost simultaneously by Brodie of Oxford and the present writer, and subsequently developed and extended by the latter, is given at length in his essay on Celestial Chemistry from the Time of Newton (15), as follows:—

"In Part I. of his *Calculus of Chemical Operations*, read before the Royal Society, May 3, 1866, and published in the *Philosophical Transactions* for that year, Brodie was led to assume the existence of certain ideal elements. These, he said, 'though now revealed

to us through the numerical properties of chemical equations only as *implicit and dependent existences*, we cannot but surmise may sometimes become, or may in the past have been, *isolated and independent existences.*' Shortly after this publication, in the spring of 1867, I spent several days in Paris with the late Henri Sainte-Claire Deville, repeating with him some of his remarkable experiments in chemical dissociation, the theory of which we then discussed in its relations to Faye's solar hypothesis. From Paris, in the month of May, I went, as the guest of Brodie, for a few days to Oxford, where I read for the first time, and discussed with him, his essay on the Calculus of Chemical Operations, in which connection occurred the very natural suggestion that his ideal elements might, perhaps, be liberated in solar fires, and thus be made evident to the spectroscope."

§ 15A. "I was then about to give, by invitation, a lecture before the Royal Institution, on The Chemistry of the Primeval Earth, which was delivered May 31, 1867. A stenographic report of the lecture, revised by the author, was published in the Chemical News of June

21, 1867, and in the Proceedings of the Royal Institution. Therein, I considered the chemistry of nebulæ, sun, and stars in the combined light of spectroscopic analysis and Deville's researches on dissociation, and concluded with the generalization that the 'breaking-up of compounds, or dissociation of elements, by intense heat is a principle of universal application, so that we may suppose that all the elements which make up the sun, or our planet, would, when so intensely heated as to be in the gaseous condition which all matter is capable of assuming, remain uncombined ; that is to say, would exist together in the state of chemical elements ; whose further dissociation in stellar or nebulous masses may even give us evidence of matter still more elemental than that revealed in the experiments of the laboratory, where we can only conjecture the compound nature of many of the so-called elementary substances' (11)."

§ 16. "The importance of this conception, in view of subsequent discoveries in spectroscopy and in stellar chemistry, has been well set forth by Lockyer, in his late lectures on Solar Phys-

ics,¹ where, however, the generalization is described as having been first made by Brodie, in 1867. A similar but later enunciation of the same idea by Clerk-Maxwell is also cited by Lockyer. Brodie, in fact, on the 6th of June, one week after my own lecture, gave a lecture on Ideal Chemistry before the Chemical Society of London, published in the Chemical News of June 14, in which, with regard to his ideal elements (in further extension of the suggestion already put forth by him in the extract above given from his paper of May 6, 1866), he says: 'We may conceive that in remote ages the temperature of matter was much higher than it is now, and that these other things [the ideal elements] existed in the state of perfect gases—separate existences—uncombined.' He further suggested, from spectroscopic evidence, that it is probable that 'we may one day, from this source, have revealed to us independent evidence of the existence of these ideal elements in the sun and stars.' During the months of June and July, 1867, I was absent on the Continent;

¹ Nature, Aug. 25, 1881, vol. xxiv. p. 396.

and this lecture of Brodie's remained wholly unknown to me until its republication in 1880, in a separate form, by its author,¹ with a preface, in which he pointed out that he had therein suggested the probable liberation of his ideal elements in the sun, referring at the same time to his paper of 1866, from which we have already quoted the only expression bearing on the possible independence of these ideal elements somewhere in time or in space."

"The above statements are necessary in order to explain why it is that I have made no reference to Sir Benjamin Brodie on the several occasions on which, in the interval between 1867 and the present time [1881], I have reiterated and enforced my views on the great significance of the hypothesis of celestial dissociation as giving rise to forms of matter more elemental than any known to us in terrestrial chemistry. The conception, as at first enunciated, in somewhat different forms, alike by Brodie and myself, was one to which we were both naturally, one might say inevitably, led, by different paths, from our respective fields of

¹ *Ideal Chemistry, a Lecture.* Macmillan, 1880.

speculation, and which each might accept as in the highest degree probable, and make, as it were, his own. I write, therefore, in no spirit of invidious rivalry with my honored and lamented friend, but simply to clear myself from the charge, which might otherwise be brought against me, of having, on various occasions within the past fourteen years, put forth and enlarged upon this conception without mentioning Sir Benjamin Brodie, whose only publication on the subject, so far as I am aware, was his lecture of 1867, unknown to me until its reprint in 1880."

§ 17. "It was at the grave of Priestley, in 1874, that I for the second time considered the doctrine of celestial dissociation, commencing with an account of the hypothesis put forward by F. W. Clarke, of Cincinnati, in January, 1873,¹ to explain the growing complexity which is observed when we compare the spectra of the white, yellow, and red stars; in which he saw evidence of a progressive evolution of chemical species, by a stoichiogenic process, from more

¹ Clarke, "Evolution and the Spectroscope," Popular Science Monthly, New York, vol. ii. p. 32.

elemental forms of matter. I then referred to the further development of this view by Lockyer, in his communication to the French Academy of Sciences in November of the same year, wherein he connected the successive appearance in celestial bodies of chemical species of higher and higher vapor-densities with the speculations of Dumas and Pettenkofer as to the composite nature of the chemical elements.¹ I next quoted from my lecture of 1867 the language already cited (on page 28), to the effect that dissociation by intense heat in stellar worlds might give us more elemental forms of matter than any known on earth. It was further suggested that the green line in the spectrum of the solar corona (which had been supposed to indicate a hitherto unknown substance, that, 'from its extension beyond even the layer of partially cooled hydrogen, must, according to the deductions of Mr. George J. Stoney, be still lighter than this gas') may be due to a 'more elemental form of matter, which, though not seen in the nebulae, is liberated by the intense heat of the solar sphere, and

¹ Lockyer, *Comptes Rendus*, Nov. 3, 1873.

may possibly correspond to the primary matter conjectured by Dumas,¹ having an equivalent weight one-fourth that of hydrogen.' (12.) The suggestion of Lavoisier, that 'hydrogen, nitrogen, and oxygen, with heat and light, might be regarded as simpler forms of matter from which all others are derived,' was also noticed in connection with the fact that the nebulae, which we conceive to be condensing into suns and planets, have hitherto shown evidences only of the presence of the first two of these elements; which, as is well known, make up a large part of the gaseous envelope of our planet, in the forms of air and aqueous vapor. With this I connected the hypothesis that our atmosphere and ocean are but portions of the universal medium which, in an attenuated form, fills the interstellar spaces; and further suggested as 'a legitimate and plausible speculation,' that 'these same nebulae and their resulting worlds may be

¹ In the paper of 1874, it was farther said in this connection: "Mention should also be made of the unknown element conjectured by Huggins to exist in some nebulae. This conception of a first matter, or *Urstoff*, has also been maintained by Hinrichs, who has put forward an argument in its favor from a consideration of the wave-lengths in the lines of the spectra of various elements."

evolved by a process of chemical condensation from this universal atmosphere, to which they would sustain a relation somewhat analogous to that of clouds and rain to the aqueous vapor around us.'"

§ 18. "These views were reiterated in the preface to a second edition of my Chemical and Geological Essays, in 1878, and again before the British Association for the Advancement of Science, at Dublin,¹ and before the French Academy of Sciences in the same year.² They were still further developed in the essay on The Chemical and Geological Relations of the Atmosphere, published in 1880 (13), in which attention was called to the important contribution to the subject by Mr. Lockyer, in his ingenious and beautiful spectroscopic studies, the results of which are embodied in his 'Discussion of the Working Hypothesis that the so-called Elements are Compound Bodies,' communicated to the Royal Society, Dec. 12, 1878. It was then remarked that the already noticed 'speculation

¹ Nature, Aug. 29, 1878, vol. xviii. p. 475.

² Comptes Rendus, Sept. 23, 1878, vol. xxxviii. p. 452.

of Lavoisier is really an anticipation of that view to which spectroscopic study has led the chemists of to-day'; while it was said that the hypothesis put forth by the writer in 1874, 'which seeks for a source of the nebulous matter itself, is, perhaps, a legitimate extension of the nebular hypothesis.'" (15.)

§ 19. That the law of chemical dissociation by heat is universal, and that in nebulous and stellar masses we may expect to find more elemental forms of matter than are known on earth, was maintained by the writer in May, 1867. In August, 1874, connecting this conception with the earlier speculations of Dumas as to the composite nature of the so-called chemical elements, and with the order of appearance of these in different classes of stars, as noticed by Clarke, it was suggested that the material from which the known elements have been generated by the stoichiogenic process, through successive condensations in cooling, is no other than the unknown element discerned by the spectroscope in the solar chromosphere, as the well known line, 1474. These views, which, as we have shown, have since been per-

sistently and repeatedly asserted by the writer, are now finding recognition among chemists, some of whom seem to overlook the history of their origin. Such a genesis of the elements is assumed by E. J. Mills, who, in 1886, writes:¹ "The cooling of the primitive matter may be regarded from a chemical point of view as resulting in a succession of polymers (1, 2, 3 . . .) n ; n being the primitive density. But, on account of the evolution of heat when a polymer is formed, there will ensue, as a physical consequence, the inversion of more or less of the cooling, and therefore of the polymerization"; a process of which it is easy to trace the history, as Mills has done, in variable stars.

§ 20. In his address before the British Association for the Advancement of Science, in September, 1886, Crookes has given a popular statement of the hypothesis of the genesis of the chemical elements from an intensely heated primal matter, during the cooling of which they have been formed by successive polymeriza-

¹ Numerics of the Elements, Part II. L., E., and D. Philos. Mag. xxi. 157.

tions. All of this he connects with Prout's hypothesis of atomic weights, and suggests that an unknown element in the solar atmosphere may be, if not the primal matter, a substance having one-half the weight of hydrogen. I had already in 1874 expressed the opinion that this substance might be the element giving the green line, 1474, of Kirchhoff, so conspicuous in the corona; of which Young¹ remarks that it would seem that "it must be something with a density far below that of hydrogen." Crookes, however, now suggests, in 1886, another element, the hypothetical helium of Frankland, which gives the yellow line D₃. Still other unknown lines have of late years been discovered in the solar spectrum, all of which may correspond to so-called elemental species developed by the stoichiogenic process; and it may be a question to which the primacy should be conceded.

¹ C. A. Young, *The Sun*, 1881; p. 232.

CHAPTER IV.

GASES, LIQUIDS, AND SOLIDS.

§ 20. AFTER noting, in 1853, that the equivalents for volatile bodies are fixed from their vapor-densities, and for "non-volatile species are generally assumed to be those quantities which sustain the simplest ratio to certain volatile ones," it was said that, "having determined the true equivalent of a species from the density of its vapor, the inquiry arises whether a definite and constant relation may not be discovered between its vapor-density and the specific gravity of a species in its solid state. Such a relation being established, and the value of the condensation in passing from a gaseous to a solid state being known, the equivalents of solids, like those of vapors, might be determined from their specific gravities." In answer to the question then asked, "What is the value of the condensation which takes place in the change from the gaseous to the solid state,

or what equivalent corresponds to a given specific gravity in any crystalline solid?" the received formulas for alum, ferrocyanid of potassium, and glucose were discussed; and it was said: "The equivalent of a crystallized species may often be a multiple of that deduced from those chemical changes which commence only with the destruction of its crystalline individuality." It was added: "There are reasons for believing that the equivalents of these species in the crystalline state correspond to some multiples of the above formulas, a question which is to be decided by an examination of the crystallization and the specific gravity of species whose equivalents are admitted to be higher."

Farther, it was said: "Favre and Silbermann from their researches on the heat evolved in fusion and solution, have been led to conclude, firstly, that crystallized salts are polymeric of these same salts in solution — that is, they are represented by formulas which are multiples of those deduced from analysis; secondly, that double salts and acid salts do not exist in solution, being produced only during crystallization; and, thirdly, that water, in crystallizing,

changes from HO to n HO, n being some whole number.¹ These conclusions are seen to be in accordance with those deduced from a consideration of the relations of density and equivalent volume. A polymerism is evident in such salts as sulphate of potash and cyanid of potassium, when their specific gravities are compared with those of alum and the ferro-cyanid."

§ 21. Passing thence to the consideration of the alcohols and their derivatives, it was remarked that several of those then known "have very nearly the same specific gravity, so that the condensation is inversely as their vapor-equivalents." It was added that, in a farther study of such bodies, "the specific gravity at their boiling-points should probably be chosen for comparison," and that we may expect to "establish a simple relation between the densities of liquids and their vapors." (4.)

§ 22. In resuming this subject in 1867, it was farther said: "There probably exists be-

Recherches sur les quantités de chaleur dégagées dans les actions chimiques et moléculaires. 1847. Comptes Rendus de l'Acad. des Sciences, xxiv. 1081-1090.

tween the true equivalent weights of non-gaseous species and their densities a relation as simple as that between the equivalent weight of gaseous species and their specific gravities." That it was possible to discover such a relation, had already been maintained in 1853, when, as we have seen, the doctrines of polymerism and of high equivalent weights for liquid and solid species had been fully set forth. The chemical relation between solids, liquids, and gases was now, however, first clearly defined as follows :

"The gas or vapor of a volatile body constitutes a species distinct from the same body in its liquid or solid state, the chemical formula of the latter being some multiple of the first ; and the liquid and solid species often [probably always] constitute two distinct species, of different equivalent weights. In the case of analogous volatile species, as the hydrocarbons and their derivatives, the equivalent weights of the liquid and solid species approximate to a constant quantity, so that the densities of those species in the case of homologous or related alcohols, acids, ethers, and glycerids,

are subject to no great variations. These non-gaseous species are generated by the chemical union or identification of a number of volumes or equivalents of the gaseous species, which number varies inversely as the density of those gaseous species." (10.)

In 1874, reverting to the conception of the polymerism exhibited in different forms of carbon and phosphorus, as maintained in 1848 (page 12), it was said: "By the comparison of these with substances known to possess a high equivalent weight, as, for example, some organic bodies, it would even be possible to fix that of these elemental species; which would certainly be found to have a very elevated equivalent, indicating a high degree of polymerism." (12.)

CHAPTER V.

THE LAW OF NUMBERS.

§ 23. THE law of numbers, which is seen in the doctrine of multiple proportions and in polymerism, received a great extension in the discovery of what have been called progressive series, made known in 1842, by James Schiel, and adopted by Ch. Gerhardt, in 1844, in his *Précis de Chimie Organique*, under the name of homologous series. This conception was by these chemists applied only to hydrocarbonaceous compounds, differing from each other by C_2H_2 , which was shown to be the common difference in the formulas of certain series of bodies having similar chemical relations.

As regards the farther extension of this principle, and the breaking-down of the distinction hitherto maintained between so-called organic chemistry and mineral chemistry, it was said by the writer, in 1852, that "we may define

organic chemistry as the chemistry of the compounds of carbon." These were then spoken of as "the carbon series"; while "the silicon series" was made to include all the known silicious compounds. (3.) Of the above definition it has been elsewhere said that, "though a commonplace to-day, it was, perhaps, then made for the first time." (16.)

(3.) In 1853 it was farther pointed out that " C_2H_2 may be compared with O_2H_2 and with O_2M_2 " (CH_2 , OH_2 , OM_2 , in the present notation); so that since species differing by $n(C_2H_2)$ may be homologous, "it may be expected that mineral species will exhibit the same relations as those of the carbon series, and the principle of homology be greatly extended in its application," as was then shown by reference to many silicates. (4.) In the same year it was also said: "The formulas of homologous bodies may be represented as series in arithmetical progression [progressive series]. The first term may be the same as the common difference," as in the hydrocarbons of the series $n(CH_2)$, or unlike the common difference, as in the ammonias NH_3 $NH_3.n(CH_2)$. "Both of these

cases are illustrated in the chemical history of mineral species"; and " M_2S_2 , M_2O_2 , and H_2O_2 may be compared with H_2C_2 ." The application of these principles was then shown at length. (5.) The members of a progressive series in which the first term is the same as the common difference may be designated as isomeric homologues; while all other progressive series are appropriately called anisomeric.

§ 24. The progressive series among gaseous species, except in some few hydrocarbons, are examples of anisomeric homologues. To these gaseous species belong all considerations as to metagenesis, from the study of which have grown up the so-called rational and structural formulas, and the theory of types. With regard to all these it is well to remember "the language of Ch. Gerhardt, that they 'are not intended to represent the arrangement of atoms, but to make evident, in the simplest and most direct manner, the relations which connect bodies with one another in their transformations.' This understood, and with these reservations, they have an important place in chemical teaching." (12.)

The new aspects revealed by the periodic law, and the discovery of the reciprocal relations between the properties and the combining weights of the elements suffice to show that the hypothesis of Prout must, at least, be greatly modified before it can be received, and help, moreover, to give a more profound significance than was before imagined to the law of numbers in chemistry.

In 1874 the writer noticed the variations in composition which J. P. Cooke, who had observed them in certain alloys, described under the name of allomerism. These alloys were then regarded as "examples of a progressive series of isomorphous compounds of antimony and zinc, of high equivalent, differing from each other by $n\text{Zn}_2$,"¹ The bearing of this conception on the recent views of Boutlerow and Schützenberger as to the apparent variability of the law of definite proportions, and on Cooke's discussion thereof,² is evident.

¹ Hunt, *Chemical and Geological Essays*, p. 447.

² *American Journal of Science* (1883), xxvi. 63, 310.

CHAPTER VI.

EQUIVALENT WEIGHTS.

§ 25. THE conception of high equivalent weights for liquid and solid species, already indicated in the extracts in §§ 20-22, was illustrated at length in 1853 and 1854, when the carbon-spars were represented in formulas as polycarbonates with from thirty to forty portions of carbon ($C=6$); and the pyroxenes, amphiboles, and feldspars as polysilicates with from thirty-two to sixty portions of silicon ($Si=7$). The equivalent weights thus provisionally adopted for these species were confessedly *minima*; and their relations to the higher numbers of which they were supposed to be fractions were left undetermined. (5, 6.) Of these elevated equivalent weights and complex formulas it was subsequently declared that they do not show "a deviation from the law of definite proportions," but are "only an expression of that law in a higher form." (10.)

§ 26. Reverting, in this connection, to what has been said in § 22, we repeat, that all liquid and solid species, so far as known, may be represented as polymers of some primary species or chemical unit. The minimum equivalent weights of these chemical units, which, by their polymerism, give rise to higher species, must often of necessity be considerable, as in the case of many of the aniline derivatives, the ammonio-cobalt compounds, and the polytungstates. Wolcott Gibbs, who shows that these latter constitute progressive series, finds the common difference, which he terms the "homologizing term," in the phosphotungstates is not less than $2(\text{WO}_3 = 464)$, and shows for these heavy polytungstates equivalent weights, not only of 5002, but, in one case, of 20,058; while for the less heavy ammonio-cobalt salts minimum equivalent weights of from 500 to 2500 are deduced. Even these elevated numbers, as we shall endeavor to show, are but fractions of the true equivalents of the crystalline polymeric solids, which, for the species under consideration, vary from about 50,000 to more than 220,000.

§ 27. The proofs which careful analytical studies have afforded of the necessarily high equivalent weights and the complex formulas of the polytungstates, polymolybdates, polyvanadates, and polyphosphates, led Wolcott Gibbs, in 1877, to designate them as salts of "complex inorganic acids," which, according to him, "form a new department of inorganic chemistry." It will be remembered that I had already, in 1853, proclaimed that the whole chemistry of solids and liquids is only intelligible when regarded as a history of just such complex inorganic acids and salts; that the distinction between organic and inorganic chemistry is no longer tenable; that the same principles of homology and polymerism are applicable alike to the bodies of the carbon series and the silicon series; that the native crystalline carbonates, or carbon-spars, are polycarbonates, with equivalent weights of not less than from 1500 to 2500; that the pyroxenes, feldspars, and tourmalines are polysilicates of equally complex constitution, and are represented by formulas which show the

¹ American Journal of Science, 1877; xiv., 61.

existence among them both of polymers, probably homologous, and of anisomeric homologues. These conceptions, all of which were explicitly set forth and defended in 1852 and 1853, underlie the writer's philosophy of the mineral kingdom, as then enunciated, and as persistently maintained to the present date. The inquiry as to the value of the unit in these polymers, and of the common difference between the successive members of these homologous series of polycarbonates and polysilicates — whether it be the simplest admissible chemical unit, or some multiple thereof — is one which will be considered in Chapter XI.

CHAPTER VII.

HARDNESS AND CHEMICAL INDIFFERENCE.

§ 28. THAT the specific gravity of solids, like that of gases and vapors, varies as their equivalent weights, will follow from the principle, already laid down in 1853, that chemical union is essentially an identification of volumes; or, in other words, a condensation of many volumes into one. The farther and very rational deduction from this principle, that the property of hardness in similarly constituted species, as well as their resistance to chemical agents, sustains a direct relation to the condensation, was first indicated in a paper by the writer, on Euphotide and Saussurite, in the American Journal of Science for 1859, wherein were discussed the physical and chemical differences of the related silicates, meionite and zoisite. In referring to this in a note, "Sur la Nature du Jade," presented to the French Academy of

Sciences in June, 1863, it was said, in comparing meionite and zoisite: "The augmentation of density, of hardness, and of chemical indifference which is seen in this last species is doubtless to be ascribed to a more elevated equivalent; or, in other words, to a more condensed molecule.¹ These different degrees of condensation, which are constantly kept in mind in the study of organic chemistry, are besides, as I have already elsewhere shown, of great importance in mineralogy, and will form the basis of a new system of classification, which will be at once chemical and natural-historical. The different rhombohedral carbon-spars, cyanite and sillimanite, hornblende and pyroxene, offer, in like manner, examples of different degrees of condensation, and, by their chemical composition, belong to series the terms of which, like those of the hydrocarbons — $n(C_2H_2)$ — are both homologues and

¹ Regarding the relations between meionite and zoisite it was said: "L'augmentation de densité, de dureté, et d'indifférence chimique qu'on remarque dans cette dernière espèce tient sans doute à un équivalent plus élevé, c'est à dire à une molécule plus condensée." *Comptes Rendus de l'Académie des Sciences*, 1863, lvi. 1256.

multiples of the first term. At the same time, each one of these silicates and carbonates belongs to another possible series, the terms of which differ by $n(M_2O_2)$, corresponding to more or less basic salts." (9.)

§ 29. These relations of physical and chemical characters to condensation were again affirmed in 1867, when, after insisting on the evidences of polymerism "in related mineral species, such as meionite and zoisite, dipyre and jadeite, hornblende and pyroxene, calcite and aragonite, opal and quartz, in the zircons of different densities, and in the various forms of titanite oxyd and of carbon," it was said: "The hardness of these isomeric or allotropic species, and their indifference to chemical reagents increase with their condensation; or, in other words, vary inversely as their empirical equivalent volumes, so that we here find a direct relation between chemical and physical properties." (10.)

§ 30. The same relation of hardness to condensation is evident throughout natural silicates, and underlies the great distinction made in the mineralogical classification of

Mohs between the order Gem, on the one hand, and the order Spar, on the other. This distinction is made still more apparent in the division which I have made the ground of tribal subdivisions running through the three sub-orders of silicates, and in each separating them into the gem-like or adamantoid type, on the one hand, and the spathoid and hydrospathoid types, on the other. Passing from these three, which are all alike essentially sparry in crystalline structure, to the phylloid or micaceous type, the significance of the varying condensation in species of this type, as regards hardness, is somewhat obscured by the eminent cleavage in one plane. The same is true, for another reason, in the colloid, vitreous, or porodic type¹ (*Porodini* of Breithaupt), the species

¹ The term porodic (German *porodisch*), from the Greek *πωρῶν*, to harden, coagulate, or make callous, was proposed by Breithaupt, in 1836 (*Handbuch der Mineralogie*, I. 324), as synonymous with the German *geronnen* (curdled or clotted), to designate amorphous, opal-like, gelatinous, or vitreous bodies, destitute of cleavage or other marks of crystalline structure; and corresponds to the term colloid, subsequently devised by Graham. Among porodic species Breithaupt included, besides colloidal sulphates, phosphates, and arsenates, such bodies as opal, serpentine, chrysocolle, allophane, tachylite,

of which—in many cases, at least—include crystalline portions belonging to sparry types. The tribal distinctions above indicated are farther noticed in § 32.

A similar relation between hardness and chemical indifference and the degree of condensation has also been pointed out by the author for the anhydrous oxyds other than silicates, and for metals and their compounds with sulphur, selenium, tellurium, arsenic, and antimony, which make up the several tribes of the sub-orders Metallometallate and Spathometallate in the great natural order of the Metallates. (16.)

§ 31. The question of the relations of chemical indifference to condensation has lately received a new and important illustration from the study of the silicates. That, while many of these are readily attacked by fluorhydric acid, some few of them resist more or less completely its action, has long been known.

and obsidian—substances alike of aqueous and of igneous origin. Besides an order, *Porodini*, he subsequently defined porodic genera in other orders. See, farther, the author's Mineral Physiology and Physiography, p. 383.

Among the latter had been noticed staurolite and zircon, and, more recently, amphibole, pyroxene, and chrysolite,—a fact of which Fouqué availed himself to separate the last two species from various feldspars and from vitreous silicates. Mr. J. B. Mackintosh, late of Columbia College, New York, and now of Lehigh University, in extending these observations, found, as he informed me, a few months since, that garnet also is indifferent to the action of the acid; a fact ascribed by me to its great condensation, which I had already concluded to be the cause of the similar indifference of the species above named. In confirmation of this view I suggested a comparison between the more condensed species epidote and spodumene, on the one hand, and the less condensed iolite and petalite, on the other; predicting the insolubility of the first two and the solubility of the last two in fluorhydric acid. This prevision was at once confirmed by Mackintosh, who has since greatly extended, and made quantitative, similar experiments on many of the more important silicates.

§ 32. In an attempt at A Natural System in

Mineralogy, in 1885 (16), there was proposed, as already noticed, for the three sub-orders into which the order of Silicates was divided, a classification into tribes, based in great part on the different degrees of condensation; and it may be said, in a few words, that the results of Mackintosh appear in all cases to verify the law of chemical indifference laid down in 1863. While the Pectolitoids, including pectolite, apophyllite, and calamine; the Protospathoids, like willemite and wollastonite; the Zeolitoids; and the various Protoperspathoids, including the feldspars, scapolites, leucite, iolite, and petalite, are more or less completely attacked and dissolved by fluorhydric acid, the Protadamantoids, like pyroxene, amphibole, and chrysolite, resist more or less completely its action. To this tribe, also, rather than to the Pectolitoids, datolite, from its great condensation and its comparative indifference to the acid solvent, appears to belong. The same indifference is observed in the Protoperadamantoids, including garnet, epidote, zoisite, axinite, spodumene, staurolite, and the tourmalines, besides idocrase and prehnite. In like manner, the Perad-

amantoids andalusite, topaz, and cyanite resist its action. Among the phylloid or micaceous silicates, which are, for the most part, though less hard than spathoids, highly condensed species, the Protophylloid talc, and the Proto-perphylloids ripidolite, margarite, zinnwaldite, and muscovite resist the action of the acid; while biotite, phlogopite, and jefferisite are but slightly attacked.

§ 33. The rate of attack under similar conditions varies greatly for different species. When a given weight of the mineral in grains of a determined size is exposed for an hour to a large excess of a dilute fluorhydric acid which fails to attack sensibly the more resisting silicates, Mackintosh finds that, in round numbers, from one to two per cent of amphibole, about five of chrysolite, from twenty-five to thirty-five of petalite, and the feldspars, albite, oligoclase, and labradorite, forty-three of orthoclase, and sixty-six of leucite are dissolved; while willemite, like the colloid species halloysite, is completely dissolved. The same is true of the colloid, opal, while artificial tridymite is also readily attacked, but quartz is more resisting

than chrysolite. In experiments on a blast-furnace slag, it was found that portions of the mass, which, on slow cooling, had passed from a vitreous or porodic condition to one of crystallinity, with a notable increase in density, had become much less soluble in the acid. The publication of the farther results of these studies, which are still in progress, and which Mackintosh has kindly communicated to me, will constitute a most important contribution to chemical mineralogy,¹ and a farther proof of the dependence of chemical indifference on condensation.

¹ They have as yet been made known only by preliminary notices,—in the *School of Mines Quarterly*, in July, 1886; in a paper by me, as yet unpublished, read to the Royal Society of Canada, May 26, 1886; and in an appendix to my recently published *Mineral Physiology and Physiography*. A more complete account, entitled “The Action of Hydrofluoric Acid on Silica and the Silicates,” was read by Mackintosh before the American Chemical Society, in New York, November 5, 1886, and appears in the new *Journal of Analytical Chemistry* for January, 1887.

CHAPTER VIII.

THE ATOMIC HYPOTHESIS.

§ 34. FROM an early time in the history of thought two distinct and opposite conceptions of the intimate nature of matter have had their partisans. The Pythagoreans taught the infinite divisibility of matter, and its continuity in a given mass,—a view held by Plato and Aristotle, and by Kant among modern masters. The opposed doctrine of the finite divisibility of matter, and the existence of ultimate material particles, or atoms, taught by Leucippus, can be traced to Phœnician, Hindoo, and, probably, to Egyptian sources. It was maintained by Epicurus and his school, was lauded by Francis Bacon, and adopted by Newton, though controverted by Descartes, Leibnitz, and Euler; and had fallen into neglect until resuscitated in this century by Dalton, in his System of Chemi-

cal Philosophy, published in 1808; since which time it has been accepted by most of the popular writers on chemistry as a necessary part of the law of definite and multiple proportions then unfolded by Dalton.¹ The kinetic hypothesis of the constitution of gases, which conceives them to consist of solid, perfectly elastic spherical particles, moving in all directions, and actuated with different degrees of velocity for different gases, first put forward by D. Bernoulli, in 1747, and adopted by many modern

¹ See, for a history of the atomic hypothesis, Daubeny, *Introduction to the Atomic Theory*, and, more concisely, Odling, *Watts's Dictionary of Chemistry*, under "Atomic Weights." Also for an extended discussion of the history of the atomic hypothesis, and the arguments for and against it, Whewell, *History of the Inductive Sciences*, vol. i. book vi. chap. 5. He there declares that its doctrines, when they "are tried upon the general range of chemical observation, prove incapable of even expressing, without self-contradiction, the laws of phenomena." "Chemical facts not only do not prove the atomic theory as a physical truth, but they are not, according to any modification yet devised of the theory, reconcilable with its scheme." He adds that "when we would assert this theory, not as a convenient hypothesis for the expression or calculation of the laws of nature, but as a philosophical truth respecting the constitution of the universe, we find ourselves checked by difficulties of reasoning which we cannot overcome, as well as by conflicting phenomena which we cannot reconcile."

physicists, was, according to Graham, resuscitated in our own time by Herepath, in 1847.¹

§ 35. In discussing, in 1853, the nature of the chemical process, as already set forth in Chapter II., it was asserted that, "as chemical combination is not a putting together of molecules, but an interpenetration of masses, the application of the atomic hypothesis to explain the law of definite proportions is wholly unnecessary." (4.) Again, it was said that, since "the volumes of the uniting species are always merged in that of the new one . . . the atomic theory, as applied by Dalton, which makes combination consist in juxtaposition, is untenable." (5.)

§ 36. "If, then, as maintained by the writer, the law of volumes is universal, and if the production of liquids and solids by the condensation of vapors is a process of chemical union or integration, giving rise to polymers the equivalent weights of which are as much more elevated as their densities are greater than those of the vapors which combine to

¹ Graham, *Chemical and Physical Researches*, p. 211, note. For a critical examination of this hypothesis, see Stallo, *The Concepts and Theories of Modern Physics*, chapters iv. vii. viii.

form them, the application of the hypothesis of atoms and molecules to explain the law of definite proportions and the chemical process is not only unnecessary but misleading. According to this hypothesis, which supposes molecules to be built up of atoms, and masses of molecules, the different ratios in unlike species between the combining weight of the chemical unit, or molecule (as deduced from analysis and from vapor-density, $H = 1.0$), and the specific gravity of the mass are supposed to represent the relative dimensions of the molecules. Hence, the values got for solids and liquids by dividing these combining weights by the specific gravity have been called 'molecular volumes.' The number of such 'chemical molecules,' required to build up a 'physical molecule' of constant volume would, according to this hypothesis, be inversely as their size. If, however, as all the phenomena of chemistry show, the formation of higher and more complex species is by condensation or integration, or, in other words, by identification of volume, and not by juxtaposition, it follows that the so-called molecular vol-

umes are really numbers representing the relative amounts of contraction of the respective substances in passing from the gaseous to the liquid or solid state, and are the reciprocals of the coefficient of condensation of the assumed chemical units," or atoms, or molecules.¹ (17.)

§ 37. Hence it was, that in discussing, in 1885, the relations of density to equivalent, while we admitted the language of the atomic hypothesis, and, in making use of the well known formula $p \div d = v$, recognized chemical units or molecules, whose equivalent or combining weights are represented by p , we were careful to say that differences in the density of solid species "are not dependent on variations in the hypothetical units adopted for convenience in calculation, but belong to the species as an integer, and correspond to a greater or less condensation of its mass; that is to say, to the identification in a constant volume of a greater or less number of these chemical units. The very terms of atom and molecule which

¹ The paper here quoted, on "The Law of Volumes in Chemistry," is reprinted in the *Chemical News* for October 26, 1886.

we apply to these imaginary units, and to the mass, are concessions to a popular terminology, and are not only inadequate but, to a certain extent, misleading when applied to chemical operations." (16.)

§ 38. The confusion which, as already pointed out (§ 11), exists in the minds of many chemists between dynamical and chemical activities, and prevents a clear conception of the nature of the chemical process, has led to the transference of the atomic or molecular hypothesis from the theory of dynamics to the theory of chemistry. The phenomena of elasticity, of the movements of gases and liquids, of temperature, of electricity, and of radiant energy, — in a word, all the manifestations which come under the head of dynamics, — are, in the opinion of many of their students, most easily explained if we suppose that the species which is the subject of these phenomena has a structure, not continuous, but made up of discrete molecules or atoms of a definite and constant size, which in liquid and solid bodies varies for different species.

§ 39. The acceptance of this hypothesis of the constitution of matter for all species,

whether solid, liquid, or gaseous, will be seen, on reflection, to have no direct bearing on chemism; which does not consider the species as such, but only its relations to the species from which it has been derived, or into which it may pass, by processes of specific integration or disintegration, either homogeneous or heterogeneous.

If it were possible to demonstrate the existence of a molecular structure, for example, in a crystal of calcite; to fix, as has been attempted, by calculation, the dimensions and the weight of the constituent molecules by the juxtaposition of which the crystal is built up, we should have no better warrant than before for the hypothesis that, in these molecules of calcite, either the unlike chemical species of carbonic dioxyd and of calcic oxyd, or those others, carbon, calcium, and oxygen, into which chemical disintegration can resolve the calcite, are present as such. "Of the relations which subsist between the higher species and those derived from them we can only assert the possibility, and, under certain conditions, the certainty of producing the one from the other." (4.)

In considering this subject in 1874 it was

said: "Are we not going beyond the limits of a sound philosophy when we endeavor by hypotheses of hard particles with void spaces, of atoms and molecules with bonds and links, to explain chemical affinities; and when we give a concrete form to our mechanical conceptions of the great laws of definite and multiple proportions to which the chemical process is subordinated? Let us not confound the image with the thing itself, until, in the language of Brodie, in the discussion of this very question, 'we mistake the suggestions of fancy for the reality of nature, and cease to distinguish between conjecture and fact.' The atomic hypothesis, by the aid of which Dalton sought to explain his great generalizations, has done good service in chemistry, as the Newtonian theory of light did in optics, but is already losing its hold on many advanced thinkers in our science." (12.)¹

¹ The reader may consult with much advantage, in this connection, a paper by C. R. A. Wright, On the Relations between the Atomic Hypothesis and the Condensed Symbolic Expressions of Chemical Facts and Changes known as Dissected (Structural) Formulæ, in 1872, L., E., and D. Philos. Mag. (4) xliii. 241-264. See, also, for R. A. Atkinson's strictures thereon, and Dr. Wright's rejoinder, *ibid.*, 428-433, 503-514.

CHAPTER IX.

THE LAW OF VOLUMES.

§ 40. "THE quantitative relation of one mineral (chemical) species to another is its equivalent weight." (10.) As regards the relation of weight to volume, it was said, in 1853: "The weights of equal volumes of gases and vapors are their equivalent weights; and the doctrine of chemical equivalents is that of the equivalency of volumes. According to the atomic hypothesis, these weights represent the relative weights of the atoms; and, as equal volumes contain the same number of atoms, these must have similar volumes, so that we come at last to the equivalency of volumes." The condensation which constitutes polymerism "evidently offers no exception to the law of equivalent volumes." (4.) Dalton, in his remarkable generalizations, which are summed up in his theory of definite and multiple proportions, "linked his

discoveries with the old hypothesis of the atomic constitution of matter, which is, however, by no means necessarily connected with the great laws of combination by weight and by number. It was reserved for Gay Lussac¹ to make known a not less beautiful generalization, by showing that in the combination of vapors and gases there exists an equally simple relation of volumes, and that measure, not less than number and weight, governs all chemical changes." "All things, declares the sage,² are ordered by measure, by number, and by weight." (12.) Already, in 1853, it had been said: "The simple relations of volume, which Gay Lussac pointed out in the chemical changes of gases, apply to all liquid and solid species, thus leading the way to a correct

¹ In his *Theory of Volumes*, *Mémoires d'Arceuil*, 1809, ii. 207.

² This is, of course, a free reading of the passage which we have chosen for the motto of this volume: "Omnia mensura, et numero, et pondere disposuisti," *Liber Sapientiae*, cap. xi., translated in the received English version of the Bible: "Thou hast ordered all things in measure, and number, and weight," *Wisdom*, xi. 20. The Greek original of this is made by Daubeney the epigraph to his *Introduction to the Atomic Theory*.

understanding of the equivalent volumes of the latter." (5.)

§ 41. We had thus in the development of a theory of chemistry clearly defined the principle that the doctrine of chemical equivalents is that of the equivalency of volumes; and that the law of volumes is universal, and applies not only to gases but to liquids and solids, which are species distinct from their corresponding vapors. We had, moreover, already, in 1853, inquired "whether a definite and constant relation may not be discovered between its vapor-density and the specific gravity of a species in its solid state," and had asked "what equivalent corresponds to a given specific gravity in any crystalline solid; or, in other words, what is the value of the condensation which takes place in the change from the gaseous to the solid state?" It was farther said: "Such a relation being established, and the value of the condensation in passing from a gaseous to a solid state being known, the equivalents of solids, like those of gases, might be determined from their specific gravities." (4.) It remains to be shown why the solution of the problem,

now offered for the first time in 1886, which seems an obvious deduction from the principles thus laid down in 1853, was not sooner discovered.

§ 42. The explanation is to be found in the fact that, while affirming in a broader sense than had before been stated the universality of the law of volumes, the writer still believed, in accordance with the generally received and as yet unquestioned teaching of those who had studied the volumetric relations of solid species, that this law was conditioned in some manner by crystalline form, so that the volume of solids (and of liquids, also) was an arbitrary and a variable quantity, instead of being, as in the case of gases and vapors, an ideal unit. The general principle laid down by Gmelin, in his Handbook of Chemistry, as deduced from the studies of the volumes of solids, is that "isomorphous substances have equal atomic volumes."¹ Otto, also, in his learned review of the subject, declares that Dumas, whose studies, in connection with Leroyer, have been the point of departure for all investigations of the

¹ Gmelin, Cavendish Society's edition, 1848, vol i.

relation between the specific gravity and the chemical composition of solids, discovered that the relation of equal volumes "is connected with the crystalline form, as it exists only in isomorphous species." He adds, in regard to the formula $p \div d = v$, "Dumas was the first to demonstrate that the value of v was sensibly the same for all bodies whose isomorphous relations had been established by Mitscherlich."¹ Following the line thus indicated, chemists have been led to compare chiefly such isomorphous groups, obtaining results which have served to confirm the belief in the correctness of this conclusion as to the significance of crystalline form.

§ 43. All this was before me in 1853, when I wrote, with regard to "some allied and isomorphous species," that "H. Kopp, in dividing the assumed equivalent weights of such bodies by their specific gravities, obtained quantities which were found to be equal for some of these related species. These numbers evidently represent the volumes of equivalents, and, in accordance

¹ Otto, Chemical Reports and Memoirs of the Cavendish Society, 1848, p. 67.

with the atomic hypothesis, are said to denote the atomic volumes." As regards the published investigations up to that time, it was then said: "Their results show that the volumes thus calculated for related species of similar crystalline form are generally identical, or sustain to each other some simple ratio." From the comparisons of the values of v in the alums and in the hydrated sodium-orthophosphates and ortharsenates, and from other examples which were apparently in accordance with the teachings of Dumas as to the identity of volume in related isomorphous species, the conclusion was then reached that "what are called the atomic volumes of crystallized species are the comparative volumes of their crystals" (4); thus stating in other terms the conclusion of Dumas that, while isomorphous substances have identical volumes, the volumes in different crystalline systems were unlike; a point of view which was then illustrated at some length. In 1855, I had more than one conference on this problem with Dumas, who had read with approval, and then discussed at length, my three papers of 1853 and 1854, while he

ingeniously explained the apparent exceptions to his law indicated in the above extracts, by the principle of polymerism.

§ 44. That some broader principle than that involved in isomorphism underlies these apparent conformities in volume was soon after perceived, though but imperfectly apprehended; and when, in 1874, the essay above quoted was republished in the writer's volume of "Chemical and Geological Essays," a foot-note was added to the portion from which was taken the above cited passage as to the relation of volume to crystalline form, saying, "The conclusions in this paragraph may be liable to correction; but I leave them as they were printed twenty-one years since." It will be noted that, in reviewing this subject in 1867, it was said: "The variable relation to space of the empirical equivalent of non-gaseous species or, in other words, the varying equivalent volume . . . shows that there exist in different species very unlike degrees of condensation" (10); no reference being made to crystalline form as in any way conditioning this condensation. The teaching of Dumas and his successors in

this field of inquiry for some years, however, maintained the writer, in common with other chemists, in the belief that the accident of crystalline form has some intimate relation with condensation. That the similar values of v in the isomorphous species compared involve a relation of equivalents not then suspected, is made apparent by the results of Graham's studies in liquid diffusion, then made known, but not fully understood even by himself; to the consideration of which we shall return in Chapter XII.

§ 45. When we have once attained the conception that the law of volumes is a fundamental and a universal law, to which all species, whether gaseous, liquid, or solid, whether colloid or crystalline, and all changes of state among these, are subordinated, the solution of the great problem proposed in 1853, and stated in § 41, is seen in the familiar processes of the conversion of water into steam and of steam into water. The latter is the change of the vapor H_2O into that polymeric liquid species which, at its maximum density, is the unit of specific gravity for all liquids and solids. According to the calculation in Ganot's *Eléments*

de Physique,¹ based on a comparison of the densities of steam as compared with air, and of air as compared with water, the ratio between the weights of equal volumes of steam at 100° and 760 mm. pressure, and of water at 0° is 1:1698. The weights of equal volumes of air and water, both at 0°, are as 1:773; but those of air at 100° and water at 0° as 0.73178:773. The density of steam at 100° and 760 mm. as compared with air under the same conditions being as 0.6225:1, it follows that the ratio between the weights of equal volumes of steam at 100° and water at 0° is as $0.73178 \times 0.6225 : 773 = 0.4555 : 773 = 1 : 1698$.

§ 46. But we may approach this question more directly, by calculating the specific gravity of steam from that of hydrogen. Regnault found for the weight of one litre of hydrogen in the latitude of Paris at 0° and 760 mm. pressure, 0.089578 gramme, which from its expansion as determined by him would at 100° be 0.065572 gramme. If we assume the equivalent of oxygen as 16.0, we have for the weight of a litre of steam, H₂O, at 100° and 760 mm., 0.590148

¹ Ganot, Atkinson's translation, fifth edition, 1872, p. 290.

gramme, and, dividing by this number the weight of one litre of water at $4^{\circ} = 1000.0$ grammes, we get 1694.49. If, however, we take for oxygen the number 15.9633 (the best figure obtainable), we have for the weight of a litre of steam at 100° and 760 mm., 0.58894 gramme, and, taking this number as the divisor, obtain 1697.96; but, as water at 0° has a specific gravity of 0.99987 (Rosetti), the ratio between steam at 100° and 760 mm. and water at 0° becomes 1 : 1697.74.

The close approximation to the directly calculated ratio 1 : 1698 got by employing the corrected equivalent weight of oxygen is such that we may assume this figure as representing the true ratio. But, in order to establish the amount of condensation in the conversion of steam into water, we must take the specific gravity of this liquid at the temperature of condensation, 100° ; and this, according to the determination of Kopp, is 0.95878.

$$1.00000 : 0.95878 :: 1698 : x = 1628.04.$$

This figure represents the number of volumes of steam at 100° and 760 mm. which are condensed in one volume of water at the same

temperature. The equivalent weight of H_2O being, according to our second calculation, not 18.0, but, more exactly, 17.9633, that of water, which is $1628(H_2O) = 29,244$.¹ In first announcing these conclusions, in September, 1886 (17), by making $H_2O = 18$, the number 29,304 was arrived at for the equivalent weight of water; and the same figure is given in the author's *Mineral Physiology and Physiography*, p. xvii. Ice is, perhaps, $1494(H_2O)$, which corresponds to a specific gravity of 0.9177.

If we take, as a close approximation, for the weight of a litre of hydrogen at 760 mm. and 0° , the ordinarily received number, 0.0896 gramme, we find for the same at 100° , 0.065588 gramme, and for water-vapor under these conditions, 0.589088 gramme. The weight of the litre of water at 100° being 958.78 grammes, we have:—

$$0.065588 : 958.78 :: 1 : x = 14,618.2.$$

Multiplying by two the value of x , which rep-

¹ This corrected value for the equivalent weight of water is given in *Science* for November 19, in an abstract of the author's communication on "A Basis for Chemistry" to the National Academy of Sciences, November 9, 1886.

resents the relation of weight between equal volumes of H_2 and water, both at 100° , we have 29,236.4, or very nearly that corresponding to $1628(H_2O) = 29,244$.

In 1885, when the problem of fixing the equivalent weights of liquid and solid species had not yet been solved, it was shown that this weight for certain solid species, such as the salts of the cobaltic ammonias, and the polytungstates, must be several thousand times that of hydrogen (§ 26), with correspondingly large equivalent volumes. Having then noticed what, in the language of the atomic theory, were called the unit-weight and the unit-volume (§ 48), represented by P and V ($=p$ and v), it was said: "The relations alike of this unit-weight and unit-volume to those of the molecule to which it belongs are unknown. But this molecule has, by our hypothesis, a constant volume, for which an expression is yet wanting, and can, so far as known, only be attained by assuming as unity the number which corresponds to the highest discovered value of V . The true unit of molecular volume will probably still be some multiple of this number." (16.)

CHAPTER X.

METAMORPHOSIS IN CHEMISTRY.

§ 47. CHEMISM may be comprehensively defined as the production of new chemical species, either by integration or by disintegration; and these changes, as has been farther shown, may be either homogeneous or heterogeneous. In heterogeneous integration two species of unlike centesimal composition unite; and in heterogeneous differentiation a species is resolved into two or more unlike ones. This genesis of complex species having a centesimal composition unlike the parents, we have designated as *metagenesis*, as set forth at some length in Chapter II. In homogeneous chemical change we have the production of new species by the union or integration of two or more like species, either elemental, or, if complex, of identical centesimal composition; or conversely, the disintegration of such com-

pounded species into simpler and like forms. These homogeneous chemical changes constitute what we have distinguished as *metamorphosis* in chemistry, and include both polymerization and depolymerization. They have long been familiar to chemists, alike in so-called elements and in many hydrocarbonaceous bodies, as has been noticed in § 5, but their importance is such as to demand a special discussion.

§ 48. It has already been shown that the bodies derived from gases and vapors by liquefaction and solidification are distinct species, and are polymers of these; their generation being by a process of homogeneous integration, or, in other words, of metamorphosis by condensation; while the vaporization of such liquids and solids is homogeneous disintegration, or metamorphosis by expansion. For all species which are said to volatilize without decomposition, — that is to say, which may be converted into vapor without heterogeneous differentiation; or which, in other words, yield thereby simpler species having the same centesimal composition as their parent, — the equivalent weights are known from

their vapor-densities; and the coefficient of condensation for such liquid and solid species is directly found by comparing the density of these gaseous species with that of their liquid and solid polymers, as already shown in the case of steam, water, and ice.

When, however, we have to deal with species which are too fixed in the fire to admit of vapor-determinations, or with those which by heat undergo heterogeneous disintegration, — as, for example, sugars, carbon-spars, and hydrous silicates, — in place of the unit-weight deduced from vapor-density (as in the case of water, mercuric chlorid, or sulphur), we may make the simplest formula deduced from analysis serve as the unit; or, for greater convenience in calculation, may, in the case of oxyds and silicates, assign to it a value corresponding to $H = 1$ and $O = 8$. The unit for silica thus becomes $SiO_2 = 60 \div 4 = 15$; that for alumina $Al_2O_3 = 102 \div 6 = 17$; and that for the magnesian silicate forsterite, $SiMg_2O_4 = 140 \div 8 = 17.5$. Such unit-weights have been employed by the writer in his late essay on *A Natural System in Mineralogy* (16), in the tables of which they have

been represented by P; while the values got by dividing these numbers by the specific gravities have been called unit-volumes, and designated by V. That the units which make up the polymers in such non-volatile species are, however, far greater than these unit-weights is apparent when we consider the highly complex formulas, and the elevated equivalent weights, to which we are led by the analyses of many species, as already noted in Chapter VI.

§ 49. To similar conclusions are we conducted by the study of the phenomena of metamorphosis in certain hydrocarbonaceous species, notable examples of which are seen in the aldehydes, and in the turpentine-oils. It will be remembered that normal acetic aldehyde, with a vapor-density corresponding to C_2H_4O and a specific gravity of about .800, boiling at 21° , is, in presence of small quantities of various reagents, such as chlorhydric acid or sulphurous anhydrid, at ordinary temperatures, rapidly converted, with considerable evolution of heat, into paraldehyde, a liquid of specific gravity .998, boiling at 124° , becoming a crystalline solid at 10° , and, from its vapor-density, a tri-aldehyde

$3(\text{C}_2\text{H}_4\text{O})$. The same reagents, at low temperatures, convert aldehyde into another modification, metaldehyde, which is a crystalline solid at 100° , and at a higher temperature volatilizes without fusion. From the readiness with which (like paraldehyde) it is, at a higher temperature, reconverted into normal aldehyde, the vapor-density of this polyaldehyde $x(\text{C}_2\text{H}_4\text{O})$ cannot be determined.

Chloral, $\text{C}_2(\text{HCl}_2)\text{O}$, in like manner, readily changes into a white insoluble species, meta-chloral, of unknown equivalent weight, which at 180° is converted into the vapor of normal chloral, volatile at 95° . Still more remarkable is the case of formic aldehyde, or methylene oxyd, at ordinary temperatures a gas soluble in water, and, as shown by its vapor-density, $\text{CH}_2\text{O}=30$, which spontaneously changes into a white, insoluble polymer. This, which is volatile at 100° , melts at 152° , and its vapor, which is perhaps $3(\text{CH}_2\text{O})$, is at a higher temperature metamorphosed into the normal aldehyde, which polymerizes again on cooling. We have thus an example of two interconvertible species of identical centesimal composition, the one a gas,

soluble in water, and the other a white insoluble solid.

§ 50. Chemists have long distinguished among the turpentine-oils a considerable number of species which, while having the same centesimal composition, differ considerably not only in chemical relations, in optical characters, and in being liquid or solid at ordinary temperatures, but in specific gravity and in boiling-point. Some of these are found in nature, while others are produced by the transformations of ordinary French or American turpentine-oil. This, to which the formula $C_{10}H_{16}$ is assigned, is readily metamorphosed by heat, and by many reagents, giving rise to a large number of new species. Some of these belong (together with various natural oils) to the class of proper turpenes, including several groups, to all of which is assigned the above formula. Among these natural and artificial turpenes are the liquid pinenes, boiling at about 160° ; the camphenes, having a similar boiling-point, but forming crystalline solids below 50° ; and the limonenes, liquids boiling about 175° – 177° , — with several other groups — each of these

including varieties or sub-species, differing in optical characters and in chemical relations. Besides these true turpenes are others, regarded as sesquiterpenes ($C_{15}H_{24}$), boiling at 250° – 260° ; diturpene, or colophene ($C_{20}H_{32}$), boiling at 300° ; and polyturpenes, of still higher equivalent and unknown complexity, boiling above 360° .

§ 51. When the vapor of turpentine-oil is passed through a tube heated to low redness, the products of condensation yield, besides different turpenes, and colophene, a considerable portion of a very volatile liquid, boiling between 37° and 40° , with a vapor-density showing it to be a hemiturpene (C_8H_8), which is designated pentine, and is apparently identical with what have been called isoprene and valerylene. Besides these homogeneous transformations or metamorphoses, both of integration and differentiation, produced by heat in turpentine-oil, there is a simultaneous heterogeneous differentiation of a portion, resulting in the production of a homologue of pentine, namely, heptene (C_7H_{12}), and probably, also, of the intermediate hexene, together with hydro-

carbons of the benzene-toluene series, and some permanent gases.

When pentine is heated in sealed tubes to 280° , it undergoes a partial polymerization, a portion of it being changed into a turpene, with a little colophene. When distilled in open vessels, the transformation of this volatile liquid into less volatile products causes the temperature of the mass to rise rapidly, without the aid of heat from without, the action sometimes becoming explosive. A similar rise of temperature is noticed in the rapid polymerization of aldehyde, and in that of ordinary turpentine-oil, which is produced by contact with sulphuric acid or with small portions of fluorid of boron.¹ Wallach, who has lately reviewed the history of the various turpentine-oils, and the products of the polymerization of pentine and turpene, has designated these as pentine (C_8H_8); di-pentine, including the various turpenes ($C_{10}H_{16}$); tri-pentine, including also

¹ See Watts, Dictionary of Chemistry, under Turpentine-Oil; also the papers of Armstrong and Tilden, Journal of the Chemical Society of London, vols. 35 and 45; and later, Wallach, Liebigs Annalen, vol. ccxxvii., p. 277.

various sub-species ($C_{15}H_{24}$); and tetra-pentine, or colophene ($C_{20}H_{32}$);—besides the higher polymers, of unknown complexity, including the so-called metaterpene. The specific gravity of pentine (mono-pentine) is about .680; that of the turpenes varies, but is not far from .850; and that of the higher polymers is from .920 to above 1.00.

§ 52. The disengagement of heat, noticed in the polymerization of aldehyde, of pentine, and of turpentine-oil, is analogous to that, resulting in vivid incandescence from internal change, which takes place when many amorphous bodies are heated to low redness, by which change, in the language of Gmelin, they acquire "greater specific gravity, greater hardness, and less solubility." This incandescence is observed in titanic, tantalic, molybdous, zirconic, chromic, and ferric oxyds, in magnesium pyrophosphate, and in certain artificial arsenates and antimonates, as well as in native minerals, like euxenite, gadolinite, and allanite. Such as these were called by Scheerer pyrognomic species, and adduced by him as evidence that the granitic veinstones in which they are

found were not formed at very elevated temperatures.¹

§ 53. We have already noticed the question of metamorphosis among so-called elemental species, as discussed in 1848 (§ 5). As regards sulphur, and the threefold condensation of its vapor then suggested, it will be remembered that, as was shown by Bineau, in 1869, this vapor, at temperatures approaching 1000° , is expanded to that of normal sulphur. To this we have a parallel in the cases of paraldehyde and metaldehyde, readily converted into aldehyde, and in turpentine-oil, itself a polymer, which may be volatilized as such, but at an elevated temperature is resolved into pentene (C_5H_8), which, as we have seen, readily passes again into $C_{10}H_{16}$, and still higher polymers.

The effect of a given temperature upon a vapor cannot be determined *a priori*; while sulphur and turpentine-oil volatilize as polymers, the vapors of which undergo homogeneous differentiation only at much higher temper-

¹ See, in this connection, Gmelin's Handbook, Cavendish Society's Edition, I. 106, 107; also the author's Mineral Physiology, etc., p. 96.

atures, the vapor of water assumes at once its normal type, H_2O , and at higher temperatures undergoes heterogeneous differentiation, or metagenesis, being resolved into hydrogen and oxygen. There are, doubtless, other gaseous polymers, which, like tri-sulphur, S_8 , and di-pentine, $2(C_5H_8)$, exist within certain limits of temperature and pressure. In this connection, the studies of Cagniard de la Tour, of Drion, and of Andrews, on the conversion of liquids into gases, are very important, and help to enlarge our conceptions of this polymerism in vapors under great pressure; while farther homogeneous integration, at lower temperatures, gives rise to liquid and solid species, more or less stable at the ordinary atmospheric pressure.

§ 54. The same gaseous species may yield two or more liquid or solid species of different degrees of density, and of different stability as well, as is evinced by differences in boiling-point. This is seen from the comparison of the various groups of liquid and solid turpenes, or di-pentines, all of which are distinct from the liquid forms alike of true pentine (mono-

pentine), of tri-pentine, and of tetra-pentine, and constitute different liquid polymers of $2(\text{C}_5\text{H}_8)$. Analogous differences are observed in the isomeric butylic alcohols, which, with a common vapor-density, exhibit, like the turpenes, considerable differences alike in specific gravity and in boiling-point, and correspond to greater or less degrees of condensation. The various di-pentines are to be compared to ice and water. The latter, under favorable conditions, is a liquid of density 1.000 (nearly), even at -10° , though then readily transformed into ice, with a density of 0.917. In like manner, we have, at ordinary temperatures, besides the unstable liquid phosphorus of density 1.77, the ordinary and readily fusible species with a density of 1.82, and the red crystalline species of density 2.35, all of which, so far as known, are directly changed by heat into the same elemental or normal vapor, without gaseous polymerism, precisely as both ice and water pass directly into the normal vapor, H_2O .

§ 55. A remarkable example of metamorphosis in an elemental species is afforded by tin, which, as observed by Fritzsche, Oudemans,

Schertel, and Richards,¹ when exposed to great natural cold, is changed from the white, tough, malleable metal, having a specific gravity of about 7.30, to a gray, brittle, crystalline body, of much less density. This change takes place not only in pure block tin but, as observed by Richards, in ingots containing 2.5 per cent of mercury, the change, at a minimum temperature of about -18° , gradually extending, in this case, from certain centres, so as in a few weeks to involve the whole mass; which had a radiated structure, and was compared in aspect to stibnite. Its density was found by Richards to be 6.175, that of the unchanged portions being 7.387. Other observers have found for this altered form, with pure tin, densities of 6.0 and even of 5.8. Its instability makes this determination difficult, since the gray, brittle species is readily changed into white tin by strong pressure, by a sudden blow, or by immersion in hot water, which restores to it its toughness and its original density of 7.30. The

¹ Watts's Dictionary of Chemistry, Third Supplement; also Richards, in Transactions American Institute of Mining Engineers, xi. 221.

gray tin exhibits, alike in acid and in alkaline liquids, electrical relations different from those of the ordinary metal.

This metamorphosis of tin is comparable to that of water into ice by cold, or that of aragonite into calcite by heat, the transformation in each case being one of homogeneous disintegration from a denser to a lighter species. It is not improbable that similar changes of state analogous to this may take place in other bodies, and that the temporary production of a similarly brittle and chemically unstable form of iron, under like circumstances, may explain the apparently ready frangibility of that metal when exposed to severe frosts.

§ 56. In 1848 (§ 5), in calling attention to the fact that sulphur-vapor in the only form then known was tri-sulphur, SSS, which was compared to SOO, it was suggested that ozone might be tri-oxygen, OOO. It however is now known that, though condensed oxygen, its equivalent weight corresponds to one-half of this, or to OOO doubled in volume by homogeneous disintegration. Making H_2 the unit of volume, we have for the vapor of tri-sulphur

S_6 , and for sulphur-vapor above 500° S_2 . If, then, normal oxygen is O_2 , ozone is not O_6 , but O_3 . So, the vapor of iodine, I_2 at temperatures approaching 1500° , is, as shown by Crafts, changed in great part into a species, I_1 , having but one-half the density which belongs to normal iodine-vapor. A similar change, to a less extent, is wrought at high temperatures in bromine and chlorine, as shown by Victor Meyer and others. These so-called elemental gaseous species thus undergo at higher temperatures a homogeneous disintegration, like that of the vapor of di-pentine, when, by heat, it is changed into pentine.

§ 57. All of these, and similar changes, are but examples of that law of dissociation by heat, which includes alike so-called elements and compounds; and, as the writer was the first to teach, in 1867, is universal, and applies to the chemistry of stellar matter. While oxygen, nitrogen, and hydrogen give no evidence of similar dissociation in our laboratories, it was then suggested that they may suffer it in the solar fires; and later, in 1874, it was pointed out that the unknown element, appar-

ently of great tenuity, shown by the spectro-scope in the solar chromosphere, as line 1474, Kirchhoff, is probably a more elemental form of matter than any known on earth, if not the primal element from which all others have been generated, as set forth at length in Chapter III. It is not improbable that the power of flame or the electric spark to effect the sudden union of chlorine and of oxygen with hydrogen may be due to the effect of intense heat in separating momentarily into simpler form portions of these gases, so that we may have in the process of their combination a union of unknown elemental and less dense species.

§ 58. Whether in any case the homogeneous differentiation or depolymerization of a volatile condensed species will be effected at a single step as, under the ordinary pressure at least, is the case with water, the alcohols, and most other liquids; or whether, as with sulphur or iodine, or with the gaseous polymers of pentene and aldehyde, by two or more successive steps, cannot, in the present state of our knowledge, be foreseen. When, therefore, we have to do with species which are not suscepti-

ble of metamorphosis by expansion, — that is to say, of integral volatilization, — we cannot, in studying their condensation, know whether we have to deal with the simplest possible formula, or with some multiple thereof. Did we not know the existence alike of monopentine, and of its polymers, dipentine, tri-pentine, and tetra-pentine, we could not tell how to write the formula of solid camphene, or of liquid isoprene, pinene, limonene, or colophene, although the equivalent weights of these had already been fixed from their specific gravities. In other words, we could not determine whether the unit by the polymerization of which these liquid and solid species have been generated is, in any given case, C_5H_8 , $C_{10}H_{16}$, $C_{15}H_{24}$, or $C_{20}H_{32}$. In like manner, we might ask whether the unit in crystalline sulphur is mono-sulphur, $S=32$, or tri-sulphur, $S_3=96$. Yet the determination of these numbers, in the one case and in the other, is necessary in order to fix the coefficient of condensation in liquid and solid species.

§ 59. Resuming here what has been said of metamorphosis, and its relations to metagen-

esis, we repeat, that the systems of structural formulas, and of types in chemistry, are but expressions of the genealogical relations of species, as deduced from a consideration of the phenomena of metagenesis. This precedes metamorphosis, which, by homogeneous integration, converts the simpler or normal species into polymeric species of higher equivalent weights. In these condensed species, as already pointed out, there is observed an increase, corresponding to the degree of condensation, in their power of resistance to chemical change; as shown in diminished volatility, fusibility, and solubility, not less than in increased hardness. Carbon dioxyd, CO_2 , is a gas, and only under exceptional conditions gives rise to liquid and solid polymers, which are rapidly depolymerized at the ordinary pressure and temperature; while the corresponding silicon dioxyd, SiO_2 , is scarcely known except in insoluble crystalline or colloidal polymeric forms, although it is probable that, at a very high temperature, it assumes the gaseous form of normal silicon dioxyd.¹

¹ In an experiment made by the writer in September, 1885, with the electrical furnace of the Messrs. Cowles, in which the

§ 60. Many complex species, when generated by double decomposition in aqueous solutions, remain dissolved for a greater or less time before separating in an insoluble condition. The interval which thus elapses before the formation of such precipitates, as in the case of ammonio-magnesium phosphate, of strontium sulphate, and of gypsum, among others, is that required to convert the soluble normal species, by homogeneous integration, into insoluble polymeric species.

Theoretically, all species may exist in their normal or soluble forms; and it is this condition which constitutes the nascent state of bodies. The manner in which oxyds like those of silicon, aluminium, and iron are not only found in nature, but are separated in our laboratories in a crystalline state from aqueous solu-

current of a dynamo-electric machine, of thirty horse-power, was passed through a horizontal column of fragments of charcoal, mingled with pure silicious sand, while a portion of this was reduced to silicon, and a still larger amount fused into a glass, a small portion was found in botryoidal masses, like chalcedony in aspect, adhering to the covering tiles of the furnace, apparently from direct volatilization. See Transactions American Institute of Mining Engineers for 1885; and Chemical News for Nov. 6, 1885; pp. 235-236.

tions, shows that these oxyds, before passing into insoluble and highly condensed polymeric forms, have, like the compounds named above, enjoyed a temporary solubility in water. The very soluble forms of silicic, titanic, stannic, tungstic, ferric, chromic, and aluminic oxyds, which were especially studied by Graham, are well known examples of this. That the mineral silicates, sulphids, etc., found in veinstones have also at one time been in similar conditions, is evident from geognostical observations.¹ This question was discussed by the present writer in 1872, when it was said that "it will probably one day be shown that for the greater number of those oxygenized compounds which we call insoluble, there exists a modification soluble in water." The tendency of most normal species to pass into polymeric or condensed forms, of greater or less stability, is a fact of fundamental importance in chemistry.

¹ Chemical and Geological Essays, page 223, *note*.

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CHAPTER XI.

THE LAW OF DENSITIES.

§ 61. THE significance of the question raised in § 58 of the last chapter will be made more apparent in considering the densities of some well known solid species; as, for example, the minerals included under the name of calcareous spar or calcite, and consisting of calcium-carbonate. In calculating, in Chapter IX., the equivalent weight of water, it has been shown that the direct determination of the ratio between the volume of water at 0° and that of steam at 100° ($=1:1698$) agrees closely with the number calculated from the density of hydrogen gas ($H=1.0$), if that of oxygen be taken at 15.9633 instead of 16.0, as formerly admitted. This correction makes, for water, into which the oxygen-value enters so largely, a noteworthy difference, and gives 29,244 instead of 29,304, as the equivalent

weight of water, 1628(H₂O). In species in which this value enters in smaller proportion, the difference is of less moment. Thus, for calcium-carbonate, CCaO₃, which, with O = 16, has a combining number of 100.0, we find, on substituting the corrected value, O = 15.9633, that the number is 99.89.

§ 62. Dividing the first combining number by 2.735, as the approximate density of calcite (water = 1.000), we get $100.0 \div 2.735 = 35.56$ as the reciprocal of the coefficient of condensation, which gives 800 as the coefficient itself; since $800 \times 35.56 = 29,248$, or almost exactly the equivalent weight of water, and consequently for the equivalent weight of calcite itself the number 80,000. Substituting the second combining number, 99.89, we obtain instead, 79,922. But, since the specific gravity is directly as the equivalent weight, we have for these two values respectively, as follows:—

$$29,244 : 80,000 :: 1 : x = 2.7325.$$

$$29,244 : 79,922 :: 1 : x = 2.7356.$$

The small difference of about .003 in these two calculations of the specific gravity of

weight of water, 1628(H₂O). In species in which this value enters in smaller proportion, the difference is of less moment. Thus, for calcium-carbonate, CCaO₃, which, with O = 16, has a combining number of 100.0, we find, on substituting the corrected value, O = 15.9633, that the number is 99.89.

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$$29,244 : 79,922 :: 1 : x = 2.7356.$$

The small difference of about .003 in these two calculations of the specific gravity of

sub-species of rhombohedral calcium-carbonate thus defined : —

Carbonites archigoni ^{us}	
Sub-species <i>C. a. levis</i>	2.690–2.710
“ <i>C. a. ponderosus</i>	2.734–2.754
Carbonites paroicus	2.652–2.678
Carbonites eugnosticus	
Sub-species <i>C. e. epithematicus</i> . .	2.700–2.708
“ <i>C. e. mediocris</i>	2.716–2.720
“ <i>C. e. hypothematicus</i> ,	2.720–2.730
Carbonites diamesus	
Sub-species <i>C. d. polymorphus</i> . .	2.707–2.714
“ <i>C. d. mediocris</i>	2.721–2.727
“ <i>C. d. syngeneticus</i>	2.732–2.749
Carbonites meroxenus	2.689–2.705
Carbonites haplotypicus	2.728–2.729
Carbonites melleus	2.695–2.697

Of these, *C. diamesus* is by far the most abundant and widely diffused species. The hardness of these calcites varies from $4\frac{1}{2}$ and 4 to $3\frac{3}{4}$ on the scale of Breithaupt, the heavier being the harder species; while the range of densities observed is from 2.652 to 2.754.

§ 65. Reverting to the law of densities already set forth, and taking $\text{CCaO}_3 = 99.89$, we arrive, for calcites of different coefficients of condensation, and for aragonite, at the densities given on the following page.

It is evident that, while the *Carbonites parvius* of Breithaupt corresponds nearly in density to 775(CCaO_3) or 780(CCOa_3), *Carbonites archigoni*, sub-species *a. ponderosus*, attains the density of 805(CCaO_3), the other calcites corresponding to some intermediate term; while that of 860(CCaO_3) agrees closely with the known density of aragonite, which was referred by Breithaupt to another genus, and according to him includes *Holoëdrites haplotypicus* and *H. alloprismaticus*.

775(CCaO_3)	2.6501
780(CCaO_3)	2.6672
790(CCaO_3)	2.7014
800(CCaO_3)	2.7356
805(CCaO_3)	2.7527
860(CCaO_3)	2.9408

§ 66. The question here arises as to the value of the polymeric unit in these calcium carbonates with densities varying from 2.652 to 2.940. In case of acetic aldehyde and the products of its metamorphosis, we are enabled by vapor-densities to show that in one case we have to do with $\text{C}_2\text{H}_4\text{O}$, and in another with $3(\text{C}_2\text{H}_4\text{O})$; while in the turpentine group

we have in liquid pentine a condensation of C_5H_8 ; the various liquid and solid di-pentines of different specific gravities and boiling-points, being in like manner condensation-products of $2(C_5H_8)$. In all of these, also, the points of fusion and of ebullition help to guide us. When, however, we come to deal with non-volatile solids, like calcite, this mode of determination is no longer open to us, and we cannot say whether in the calcites the unit is $CCaO_3$ or a multiple thereof by two, five, or ten; whether, in short, the formula for the calcite of density 2.7356 is to be written $800(CCaO_3)$, $400(C_2Ca_2O_6)$, $160(C_5Ca_5O_{15})$, or $80(C_{10}Ca_{10}O_{30})$. Could we observe sharply marked intervals in the density of various calcites, corresponding to certain multiples of $CCaO_3$, they would furnish the data for the determination of the problem. But in this case we may, from the absence of such intervals, infer the probable intervention of the principle of crystalline admixtures among isomorphous species, giving rise to calcites of intermediate densities. This principle, first clearly applied in mineralogy by Von Walters-

hausen, in 1853, and by the writer, more fully, and independently, in 1854 (6), is of importance within the limits then assigned to it; though, as has been elsewhere shown, its application has been misconceived by Tschermak, who some years afterwards adopted it.¹

§ 67. In the equation $p \div d = v$, it will be noted that the value of p is, for all gaseous or volatile species, deduced directly from the observed density of the gas or vapor, and represents the specific gravity of such species, hydrogen gas being unity ($H_2 = 2.0$); the same value, for non-volatile species, being assumed as corresponding or equivalent thereto. As examples, for the gaseous carbon dioxide CO_2 , we find $p = 44$ ($O = 16$); while for the related silicon dioxide, SiO_2 , which has only been observed in solid, dense, polymeric forms, such as quartz and tridymite, we assume $p = 60$, which is the equivalent weight of the unknown normal gaseous silicon dioxide. For calcite, in like manner, we assume the formula $CCaO_3$, with a value for p 100, which is the equivalent

¹ See Mineral Physiology and Physiography, pp. 294-296, 342.

lent weight of a gas or vapor less dense than that of amylic alcohol.

On the other hand, d represents the density as computed for liquids and solids; for all of which that of water at 4° is taken as unity. The relation $d : p$ is, then, that of the density of water to that of hydrogen gas, — the two units of specific gravity, — or, in general terms, is that of liquid and solid to that of gas and vapor; while v shows the contraction in passing from the gaseous to the liquid or solid state or, in other words, is the reciprocal of the coefficient of condensation. For water, in which the value of $d = 1.000$, it is evident that $d = v$, or, in other words, that the reciprocal is identical with the gaseous equivalent weight. We have selected water as the first example, precisely because its specific gravity at $4^{\circ} (= 1.000)$ is made the unit of density for all liquids and solids; from which it follows that the equivalent weight of its vapor, p (which is its specific gravity, $H = 1.000$), and its reciprocal of condensation, v (taking now the corrected equivalent weight of oxygen $= 15.9633$) are alike 17.9633. In the case of ice, however, if we

take $d = 0.917$, we have $v = 19.5888$. We thus obtain :—

$$\begin{aligned} \text{Water} &= 1628(\text{H}_2\text{O}) \quad . \quad . \quad 1628 \times 17.9633 = 29,244 \\ \text{Ice} &= 1492(\text{H}_2\text{O}) \quad . \quad . \quad . \quad 1492 \times 19.5888 = 29,246 \end{aligned}$$

§ 68. The question to be settled in fixing the equivalent of water is to know its specific gravity as compared with that of the same volume of hydrogen gas, or of steam, at a common temperature, and at the standard pressure; for which experiment has accurately determined the weight of these elastic fluids. These relations are conveniently shown in the following table :—

SPECIES.	FORMULA.	GRAMS IN 1 LITRE 100° and 760 mm.	EQUIVALENT WEIGHT.
Hydrogen	H ₂	0.065572	2.0000
Steam	H ₂ O	0.58940	17.9633
Water	1628(H ₂ O)	958.780000	29,244.0000

It will be remembered that the contraction of water in cooling from 100° to 4° suffices to raise the weight of the litre to 1000 grams.

§ 69. To give a farther illustration: the hydrocarbon vapor butane, C₄H₁₀ = 58, con-

denses below 10° to a liquid having at 0° an observed specific gravity of 0.600, which corresponds to an equivalent weight of 17,546, compared with water as 29,244. This is not far from $302(\text{C}_4\text{H}_{10}) = 17,516$, which, at its point of ebullition, should have a specific gravity of 0.5989. While the reciprocal of the coefficient of condensation for steam, $v = 17.9633$, that for the gaseous hydrocarbon butane, with its observed density, is

$$0.600 : 1.000 :: 58 : v = 96.66.$$

The value v in the formula $p \div d = v$, being the reciprocal of the coefficient of the condensation suffered by the gaseous species (or the hypothetical unit), having its combining weight (or, in other words, its specific gravity, hydrogen gas being unity) represented by p , in passing to a specific gravity calculated for water at 4° as unity, and represented by d . We may, therefore, for brevity, designate the value v thus calculated for the condensed species as its *reciprocal number*.

The density of solids, as of liquid species, should for comparison, as already pointed out in

1853 (§ 21), be taken at the temperature of their formation, or, rather, at the highest temperature which they will sustain without chemical change. This point is, however, difficult to fix for many solids; and, as the coefficient of expansion varies for different species, and is at most not very considerable, we take, for the present purposes of study, the densities of these as already determined at ordinary temperatures.

CHAPTER XII.

A HISTORICAL RETROSPECT.

§ 70. OF the fundamental conceptions embodied in the scheme of chemical philosophy set forth in the preceding pages, there are two which have a historic interest apart from the record of them in the writer's earlier papers. These are: (1.) The doctrine of high equivalent weights and complex formulas for all liquid and solid species, dependent on homogeneous integration or so-called polymerization, and the direct connection of this, not only with hardness and insolubility, or chemical indifference, but with specific gravity; which, it has been maintained, varies for liquids and solids, as well as for gases and vapors, directly as the equivalent weight. (2.) The doctrine that liquefaction, solidification, vaporization, and the condensation of vapors, as well as solution,—in short, all changes of state in

inorganic species, —are chemical changes. It is proposed in the present chapter to notice how far these conceptions have been entertained, and to what extent they have been advanced, by others previous to or during the period of the development of the scheme which, after a growth of thirty-eight years, is now for the first time resumed and stated in a completed form.

§ 71. The conceptions of high equivalent weights and of polymerism in solid species, as deductions from thermo-chemical studies, were indicated in a general way by Favre and Silbermann, in 1847, whose conclusions were cited by the writer in his more detailed exposition of the view, in 1853 (§ 20). Graham, also, clearly stated the notion of such polymers, though only as existing in solutions, in 1849, as a deduction from his studies in diffusion, as will be shown farther on, in § 83. Their existence was maintained on other grounds, by the writer, for liquid and in solid species, both complex and elemental, in 1848, and again in 1853, 1867, and 1874, as already recounted in preceding chapters.

Spencer Pickering, who does not seem to be aware of their previous history, has set forth similar views, but only so far as regards polymerism, and the consequent high equivalent weights, in an essay on *The Molecular Weights of Liquids and Solids*, in 1885.¹ Therein, after declaring that "considerations based on the crystalline form and other physical properties of bodies force upon us the conclusion that liquid and solid molecules are in all probability of a very complicated nature, — certainly, more complex than gaseous molecules," — he writes that "the molecule of the chemist is not necessarily identical with the molecule of the physicist"; and supposes that chemical molecules may "agglomerate and act in unison as regards certain physical forces." That such an "agglomerate does not act as a unit towards chemical forces" shows, according to Pickering, that "the force which unites the individuals constituting it is not chemical force, or is chemical force of such a weak nature" as to oppose no

¹ Proceedings of British Association for the Advancement of Science, in the *Chemical News* for November 13 and 20, 1885.

perceptible resistance to ordinary chemical agents. We have here, in a mechanical form, and in the language of the atomic hypothesis, a reproduction of the views put forward by the present writer, in his early paper of 1853, as to the polymerism and high equivalent weight of liquid and solid species.

§ 72. Pickering's paper was presented to the British Association for the Advancement of Science in 1885, at the same time with one by Guthrie on Physical Molecular Equivalents. He therein calls attention to bodies previously studied by himself, and designated by him as cryohydrates and subcryohydrates; which may be described as very fusible, definite crystalline compounds, containing many portions of H_2O to a single portion of a salt or alkaloid. In these potassium nitrate is said to be combined with $44.6(H_2O)$, and potassium sulphate with $114.2(H_2O)$; while diethylamine forms a well defined and crystalline compound with $27(H_2O)$. Guthrie conceives that in these compounds the "constituents are not in the ratio of any simple multiples of their chemical equivalents." A similar conception is by him

extended to certain metallic alloys, which, from their ready fusibility, he designates, like these cryohydrates, as "eutectic."¹

§ 73. On the other hand, Messrs. Tilden and Shenstone, in their studies of the great solubility in water of salts when near their melting-points, have described compounds which, unlike the cryohydrates, are homogeneous liquids, containing, in the case of somewhat fusible compounds, like silver nitrate and benzoic acid, very small proportions of water; from which the experimenters are led to conjecture for bodies an indefinite solubility in water under proper conditions of temperature and pressure.² It is, however, easy to understand from the high equivalent weights of such dense liquids (which from their viscosity are probably colloidal) that compounds with water may exist in which the proportion of the latter, though definite, is so small a fraction that it would be neglected in the ordinary processes of analysis.

¹ Fred. Guthrie, on Physical Molecular Equivalents, *Nature*, Nov. 6, 1885; also on Eutexia, *L., E., and D. Philosophical Magazine*, 1884, xvii. 262.

² *Philosophical Transactions*, 1884; part I., pp. 23-36.

The subject of these compounds is discussed by the writer in his *Mineral Physiology and Physiography*, pp. 221-222, and also p. 245, *note*; where the geological significance of small portions of water in combination under high pressure in molten silicated rocks is insisted upon.

These two cases of apparently homogeneous compounds, — on the one hand, liquids existing at high temperatures, with very small proportions, and, on the other, solids at low temperatures, with very large proportions of water, — are like illustrations of the complex formulas and high equivalent weights which we have so long maintained. So far from being, as conjectured by Pickering, and by Guthrie, compounds in some sense outside of the domain of chemistry, their constitution, as was said of similar cases in 1867, does not present “a deviation from the law of definite proportions,” but “is only an expression of that law in a higher form.” (10.)

§ 74. A broader view, and a more complete comprehension of the great problem under consideration, is shown in a remarkable paper by Professor Louis Henry, of the Catholic Univer-

sity of Louvain, published in August, 1885, on The Polymerization of Metallic Oxyds,¹ in which, though without any reference to the present writer's publications, will be found developed alike the conception of polymerism in liquid and solid species, and the dependence thereon, not only of hardness and chemical indifference, but of specific gravity. In fact, most of the important conclusions announced in the author's publications from 1848 to 1867, inclusive, are set forth in the language of the atomic hypothesis by Henry in his recent paper.

He explains the generation of complex oxyds by the union of several equivalents of hydrates, and the successive elimination of equivalents of water, as taught by Adolphe Wurtz in 1860, in discussing the origin of polysilicates.²

¹ London, Edinburgh, and Dublin Philosophical Magazine (5) xx. 81-117. This essay escaped the notice of the writer until October, 1886; otherwise it would have been noticed in referring in Science for Sept. 10, 1886, to the paper of Spencer Pickering, when the mode of fixing the value of the coefficient of condensation for liquids and solids was first set forth, as shown in § 46.

² See the author's Mineral Physiology and Physiography, p. 298.

While the chlorids of carbon, silicon, titanium, and aluminium are species readily converted into vapors of normal density; and while carbonic dioxyd is a gas, only changed into a liquid form under great pressure, the oxyds of silicon, titanium, and aluminium are fixed and solid bodies, of greater or less density and hardness, and are polymers of the elemental oxyds. These, in their more highly condensed forms, "show a greater resistance to the action of chemical agents than in their former condition, in some cases even entirely resisting the action of acids and alkalies." Henry concludes that "the true oxyds, which are really comparable with the chlorids, are unknown, and that we possess only polymers of these, $(RO_x)_n$." The condensation of these varies, "but appears to attain its maximum in certain fixed and very infusible oxyds, such as silica, alumina, etc. . . . This enormous condensation of their molecules may possibly be the cause of the greater resistance which they offer to the action of simple chemical agents, such as hydrogen, carbon, sulphur, etc."

§ 75. Henry next suggests that "the specific

gravity of a solid body doubtless depends in a great measure on the state of aggregation, and is also intimately connected with the composition of the body, and the size of the molecular weight"; adding "the density then is, to a certain degree, a function of the molecular weight." Having reached this point, he proceeds as follows: "What, now, is the true value of the coefficient n of polymerization? What is the real molecular formula of these polymeric oxyds? These questions are, doubtless, of great interest; but it should be stated at once that it is absolutely impossible to give a direct answer. I do not know of any fact which would allow us to assign an absolute value to the coefficient n of polymerization. . . . So far as facts will permit a conclusion, we may affirm that in most cases this number is very high, although different for different oxyds."

§ 76. The problem of the value of the condensation in passing from the gaseous to the solid state, as presented by Henry, in 1885, is thus precisely that put forth by the present writer in 1853, when he asked for a determination of the coefficient of condensation, and at

the same time affirmed more positively than is done by his successor in 1885, that the density in liquids and solids varies directly as the equivalent or so-called molecular weight. (§ 41.) The direct relations of this condensation to hardness, and to chemical indifference, were, moreover, as we have seen in preceding chapters, clearly formulated by the present writer, in 1863, and even in 1848 were suggested in the case of the forms of phosphorus, etc. The problem of fixing the coefficient of condensation thus put forth, although not answered, in 1853, and again propounded, and declared unsolved, by Henry, in 1885,¹ has, it is believed, been successfully resolved in the preceding chapters.

¹ Henry has given, in his paper, the following valuable classification of oxyds, considered with reference to polymerization :—

- A. Normal oxyds, as SO_2 , CO_2 , NO .
- B. Polymerized oxyds, consisting of n molecules of the normal oxyds united.
 - i. Volatile oxyds, totally depolymerized by heating, and converted into the normal oxyd.
 - a. Completely depolymerized on volatilization, and yielding a vapor of normal density, as SO_3 , OsO_4 , methylene oxyd $(\text{CH}_2\text{O})_n$, metaldehyde $(\text{C}_2\text{H}_4\text{O})_3$.

§ 77. We must here notice an essay which appeared in 1876, entitled *Geometrical Chemistry*, by Prof. Henry Wurtz,¹ of New York, in which he insists on the great significance of density, and of the variations therein, as observed in liquid and solid species. He asserts (evidently excepting the temporary changes which depend on variations in temperature)

δ. Incompletely depolymerized at the moment of volatilization, the process being completed progressively, as the temperature rises. The vapor-density of these gradually diminishes with increase of temperature, up to a certain point, beyond which it becomes constant, and corresponds to the normal oxyds; N_2O_4 , fatty acids, and paraldehyde, which last, at low temperatures, corresponds to $(C_2H_4O)_3$, but at higher temperatures becomes (C_2H_4O) . [In this category, we may place the elemental species iodine, bromine, and chlorine.]

2. Volatile oxyds, incompletely depolymerized at temperatures to which they have been subjected, as $(As_2O_3)_2$. The volatilization of solid arsenious oxyd, at 200° , without fusion, is the change of $(As_2O_3)_n$ into $(As_2O_3)_2$.

3. Oxyds not capable of depolymerization.

a. Fixed oxyds, like SiO_2 , MgO , Al_2O_3 , Fe_2O_3 .

δ. Oxyds volatile or decomposed by heat, as HgO , Ag_2O , MnO_2 , CrO_3 ; also, organic oxyds decomposed by heating.

¹ *Geometrical Chemistry*, by Henry Wurtz, pp. 73, reprinted from the *American Chemist* for March, 1876.

that "change of volume or of density in a specific liquid, or a specifically solid body, whether elementary or compound, — even when occurring without change of crystalline system, — is an infallible indication of change of molecular structure, and, consequently, of chemical nature." Without attempting to grapple with the problem of the direct relation of density in such bodies to their equivalent weights, as propounded by the writer in 1853, and again by Louis Henry in 1885, Wurtz, nevertheless, sought to frame, in accordance with the atomic hypothesis, an explanation of the densities of liquid and solid species. To this end he constructed for these chemical formulas, which, from their frequent complexity, seem to imply polymerism and high equivalent weights. We find, however, on farther examination, that the weights adopted by him do not represent those deducible from these formulas, but are the simplest combining numbers, — hydrogen being unity, — multiplied, however, by 1000, to avoid fractions.

§ 78. Regarding chemical species as built up by the agglomeration or juxtaposition of ele-

mental molecules, Wurtz supposes that similar molecules entering into a compound may possess unlike volumes, and to this attributes the variations in the density of isomeric species. The elemental molecules in his hypothesis have different diameters, represented by integers from 12 to 40, the cubes of these numbers being the volumes of the molecules. These diameters for the metals, hydrogen, and phosphorus, are very variable; while for sulphur, chlorine, bromine, and iodine, they are pretty constantly 28 or 24; the latter being the diameter for chlorine in chlorates and in all monad or dyad chlorids. This being conceded, he applies to any liquid or solid species the formula $p \div d = v$, and thus gets what has been called its molecular volume, multiplied, like its combining weight p , by 1000. Taking now as an example, liquid chlorhydric acid, with a combining weight for $\text{HCl} = p = 36,500$, and an observed density of 1.27, we get $v = 28,516$. Deducting from this the volume of $\text{Cl} = 24^3 = 13,824$, there remains for the volume of $\text{H} = 14,692$, which, as he notes, is "almost identical with the mean figure between 24^3 and 25^3 ," whence

he concludes that "liquid hydrochloric acid must be H_2Cl_2 , containing H with the two diameters 24 and 25," and that its "volumic or molecular formula" must be represented accordingly. But the volume, as deduced from this formula $= (24^3 \times 3) + (25^3) = 57,097$, is, as near as the method will admit, double the value of v ; so that the "molecular formula," as understood by Wurtz, corresponds not to H_2Cl_2 , with two diameters for the two molecules of H , but to a mean between HCl with $H = 24$ and HCl with $H = 25$.

§ 79. In like manner, sodium chlorid with density 2.25 is represented by NaCl, in which the diameter of the molecule of sodium = 23; while that with density 2.18 is supposed to be represented by Na_2Cl_2 , in which we have sodium with the two diameters of 23 and 24. The same chlorid with density 2.05 is Na_2Cl_2 , having for sodium the two diameters 24 and 25; potassium chlorid, with density 2.01, being K_2Cl_2 , with the diameters 28 and 29 for the two potassium molecules. Similarly, phosphorus with density 1.797 is supposed to consist of one molecule with a diameter of 25, and five

molecules with a diameter of 26; while metalloid phosphorus, with density 2.297, includes one molecule of 23 and four of 24. In these cases of apparently complex formulas, however, as in the case of chlorhydric acid, the value adopted for p is not a multiple, but the number representing NaCl or P. Thus, for metalloid phosphorus, described above as made up of five molecules of P, and with a density of 2.297, we have, with $p = 31,000$, a value for $v = 13,495$. But $(24^3) \times 4 + (23^3) = 67,463 \div 5 = v = 13,492$; while $p \div v = d = 2.297$, the observed density.

§ 80. By thus adding together at pleasure the cubes of any number of integers between 12 and 40, and dividing the sum by this number, in order to obtain a mean value wherewith to divide the combining weight of the species, it is evident that we may arrive at a near approximation to the value of v as found for any observed density of a given species, and therefrom get by calculation a closely corresponding density. The assumption, however, that v represents the volume of the composite molecule generated by the putting together of

elemental molecules is, as we have sought to show, unfounded; while the other assumption that the diameters of these are represented by the integers above indicated is gratuitous. There is no apparent relation in the nature of things between these integers and the amount of contraction suffered, for example, by the gaseous species HCl, with a specific gravity = 36.5 (hydrogen being unity), in passing into the liquid species, having a specific gravity of 1.27 (water being unity); and we must regard the calculations of density, and of chemical constitution, arrived at by the above method as illusory and essentially fallacious.

Moreover, as we have elsewhere said, while calling attention to the importance of the study of the densities of liquids and solids, so well insisted upon by Wurtz, "the conception that the chemical elements enter as such into combination, and there retain their volumes, appears to be inadmissible in chemical philosophy." (16.)

§ 81. Proceeding now to consider the history of the conception that all changes of state, such as solution, fusion, solidification, vaporiza-

tion, and the condensation of vapors, are chemical in their nature, we are led to review the phenomena of gaseous and liquid diffusion, as definitely set forth by Graham, in 1849. The diffusion of salts from their solutions into pure water was by him compared to the diffusion of gases, and to the evaporation of liquids into the atmosphere. "The analogy of liquid diffusion to gaseous diffusion is borne out in every character of the former which has been examined," according to Graham; while diffusion was farther said to be "a property of a fundamental character, upon which other properties depend, like the volatility of substances." "The number of species that are soluble, and therefore diffusible, appears to be much greater than the number of volatile bodies." "Separations, both mechanical and chemical (decompositions), are produced by liquid, as well as by gaseous diffusion." "Liquid diffusion, as well as gaseous evaporation, may produce chemical decompositions." "The diffusion of a salt appears to try its tendencies to decomposition very severely."

§ 82. The above citations are from Graham's

Bakerian Lecture on Diffusion, in 1849. From his extended studies of this subject up to that date, he was led to conclude that there exist groups of equi-diffusive substances, which coincide, in many cases, with the isomorphous groups, but, on the whole, are more comprehensive than the latter. Moreover, for several groups of salts, it was found that the squares of the times of equal diffusion from solutions of the same strength stand to each other in a simple numerical relation. The squares of the times of equal diffusion of gases, as Graham had shown, are to one another in the ratio of their densities. From this, by analogy, he inferred that the molecules of these several salts, as they exist in solution, possess densities which are to one another as the squares of their times of diffusion. These he called their *solution-densities*, which, for the sulphate, nitrate, and hydrate of potassium, for example, were found to be as $4:2:1$; being the squares of 2, 1.4142 and 1, the numbers representing the relative times occupied in the diffusion of equal weights of these three species.

§ 83. Graham thus constructed a scale of

solution-densities which, in his words, "are suggested by the different diffusibilities of salts, and to which alone, guided by the analogies of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities for a new kind of molecules, but [supplies] nothing more about them." "The fact that the relations in diffusion of different substances refer to equal weights of these substances, and not to their atomic weights or equivalents, is one that reaches to the very bases of molecular chemistry. The relation most frequently perceived is that of equality. In liquid diffusion we appear to deal no longer with chemical equivalents, or the Daltonian atoms, but with masses even more simply related than these in weight. Founding still upon the chemical atoms, we may suppose that they can group themselves together in such numbers as to form new and larger molecules, of equal weight for different substances; or, if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appears to play a part in solubility, and in liquid diffu-

sion, and not the atoms of chemical combination."

The reader can judge how far this generalization of Graham, as to an apparent polymerization of species in solution, deduced from their relative rates of aqueous diffusion, led the writer naturally to the broader doctrine of polymerization alike in liquid and solid species, as put forth by him in 1853, and again in 1867. Here, also, is the view, reiterated by Spencer Pickering, of the formation of physical molecules by the union of many chemical molecules.

§ 84. Continuing his studies in diffusion, Graham wrote farther, in 1861: "So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it," — a conception fully realized in his admirable researches, published at the time, on Liquid Diffusion applied to Analysis. He added: "The range in the degree of diffusible mobility exhibited by different substances appears to be as wide as the scale of vapor-densities." Of potassium hydrate it was then said that it has double the velocity

of diffusion of potassium sulphate, and this double that of sugar, alcohol, and magnesium sulphate; all of which, however, as regards diffusion, he compared to the more volatile bodies — the comparatively fixed, or non-volatile bodies, being represented by the colloids. Of these he remarks that, "while the rigidity of crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself." "Colloids are characterized by mutability." "Their existence is a continual metastasis."¹ His conjecture that colloids have perhaps a higher equivalent weight than crystalloids, has apparently no substantial basis. We have elsewhere (§ 30) noticed the earlier observations of Breithaupt on colloids, both of aqueous and igneous origin, called by him porodic bodies. The relation of such substances to the process of diffusion was, however, unknown to Breithaupt, and was discovered by Graham.

¹ The papers of Graham above cited, published in the Philosophical Transactions for 1830 and 1861, are reprinted in his *Chemical and Physical Researches*, 1876, pp. 444-600.

§ 85. As early as 1847, in a paper already noticed (§ 20), Favre and Silbermann¹ had described the loss and fixation of water in the efflorescence and deliquescence caused by the action of the atmosphere on certain bodies, and the precipitation by heat of anhydrous sodium sulphate from its aqueous solution, as alike chemical processes. As facts in the same order, Graham had shown, in 1849, that both liquid and gaseous diffusion may produce chemical decomposition, and had compared these processes to volatilization. It was reserved for Henri Sainte-Claire Deville to take another step in this new way by his studies in chemical dissociation, the publication of which was begun in 1857, when he described the decomposition by heat of potassium hydrate, and showed the partial decomposition of water at temperatures much lower than had hitherto been suspected.² In 1860, he said of dissociations by heat, that we are "authorized in assimilating these phenomena to those of the ebulli-

¹ *Comptes Rendus de l'Acad. des Sciences*, 1847, xxiv. 1081-1090.

² *Ibid.*, 1857; xlv. 857.

tion of liquids, or the vaporization of non-liquefiable solids." ¹ The action of metallic points in promoting ebullition was then by him compared to that of manganese oxyd in fused potassium chlorate.

§ 86. Returning to the subject in 1863,² in farther discussion of the decomposition of water by heat, Deville wrote: "The comparisons between the effects of *cohesion* and of *affinity*, which are so instructive for liquid and solid bodies, are maintained in the inverse phenomena of *volatilization* and *decomposition*. Admitting this comparison, we see that the phenomena of the decomposition of bodies at a relatively low temperature, or dissociation, corresponds to the vaporization of a liquid at a temperature below its boiling-point; and that the quantity of the body dissociated at a given temperature will be proportional to its tension of dissociation expressed in millimetres of mercury; as the quantity of vapor formed above a liquid at a given temperature is proportional to the maximum tension of

¹ L., E., and D. Philos. Mag., 1860; xx. 457.

² Comptes Rendus de l'Acad., 1863; lvi. 195-201.

its vapor." "The phenomenon of the decomposition of bodies is in all respects similar to that of the ebullition of liquids, the principal character of which is the invariability of their temperature, whatever the intensity of the source of heat, provided the pressure is constant."

Thus, while looking upon the cohesion of liquids, and their volatilization, as phenomena in some way distinct from those of chemical combination and decomposition, Deville was forced to conclude that they are governed by the same laws; involving a change of state and of thermic relations, and subordinated to the same conditions of temperature and of pressure.

§ 87. In considering, in 1863, the phenomena of dissociation, as then lately studied by Pébal for ammonium chlorid, and by Wanklyn and Robinson for sulphuric acid and phosphorus chlorid, Deville recalls the phenomena of diffusion, as studied by Graham in aqueous solutions, and adds: We have here "a veritable force which leads to the separation of elements, and which must not be neglected in the explanation of the phenomena described by Messrs. Pébal, Wanklyn, and Robinson, since

the same reasoning applies to aqueous diffusion and to diffusion in gases or vapors which have different diffusive powers or rates of transpiration. The new agent of decomposition introduced by Graham is so energetic that we can no longer designate as spontaneous the decompositions produced under its influence."¹

Still later, in 1865,² Deville wrote of chemical combination: "We have no knowledge of what combination is; we do not even know what distinguishes it from solution; but we can characterize it as a change of state, marked by new physical or chemical properties, serving to distinguish combination from simple mixture. This change of state is most generally accompanied by a disengagement of latent heat, which approximates combination to the condensation of vapors; but it may also be accompanied by an absorption of latent heat, or cooling, as for explosive bodies like NO and NCl₃, which are formed by combination in the nascent state, and give off heat in decomposing; so that the

¹ *Comptes Rendus de l'Acad.*, April 20, 1863; lvi. pp. 729-733.

² *Bulletin de la Société Chimique*; iii. 15.

disengagement of heat, the production of cold, or the absence of thermometric effect, proves nothing for or against the fact of combination."

§ 88. Thus we have seen that Favre and Silbermann, in 1847, regarded the separation of salts from solutions by changes of temperature, the fixation of aqueous vapor from the atmosphere by certain bodies, and its loss by others, as all alike chemical changes. Graham, in 1849, insisted upon the likeness of the volatilization of liquids to gaseous and liquid diffusion, and asserted that all of these processes may produce chemical decompositions. Henri Sainte-Claire Deville, in 1857-1863, while adopting Graham's conclusions, farther declared that the decomposition of bodies by heat is in all respects similar to that of the evaporation of liquids, and is subordinated to the same laws.

§ 89. The writer, who enjoyed the great advantage of personal intercourse alike with Graham and with Sainte-Claire Deville, and conversed with both of them on the subjects here discussed, had with the latter, whom he had then long known, frequent conferences during the

spring and summer of 1867, at his laboratory, at the École Normale, in Paris, when the relations of the homogeneous volatilization of liquids and solids were compared with the phenomena of dissociation. Graham, whom I had known since 1856, was there for a few days our companion; and to both of these I maintained, in accordance with the views in my paper, then recently published (10), that the liquid and solid bodies, water and ice, are polymeric species, distinct from aqueous vapor, their conversion into which is a process of depolymerization, or homogeneous disintegration; a conclusion admitted by both Graham and Deville to be a logical deduction from their own premises, as has already been shown. The views which I have advocated in various publications since 1853, and in the preceding chapters, with regard to the constitution of liquids and solids, their high equivalent weights, and all their relations to gases and vapors, appear to be in fact but the legitimate and necessary consequences of those first put forward by Favre and Silbermann, and continued by Graham, Deville, and myself.

CHAPTER XIII.

CONCLUSIONS.

§ 90. THE views maintained in the preceding chapters as a basis for a philosophy of chemistry, may be resumed as follows :—

The chemical process may be defined as the integration or the disintegration of chemical species, resulting in the production of new species, also chemical. Both of these changes may be either homogeneous or heterogeneous; that is to say, the species concerned therein may be elementary, or, if complex, may be like or unlike in centesimal composition.

The generation, by heterogeneous change, of species dissimilar to the parents we have designated metagenesis. In heterogeneous integration two or more unlike species combine to form a new one, and in heterogeneous disintegration a species separates into two or more unlike to each other. The union of hydrogen and carbon to form acetylene, of oxygen and

carbon to form carbon dioxyd, the absorption of the latter by sodium hydrate, or of atmospheric water by calcium chlorid, are examples of heterogeneous integration. The loss of water in the evaporation of a saline solution, in the efflorescence of hydrated sodium carbonate, and the disengagement of carbon dioxyd by heat from calcium carbonate, are, in like manner, examples of heterogeneous disintegration. All solution is heterogeneous integration; while the separation of crystals from a solution is heterogeneous disintegration.

What is called double decomposition consists in heterogeneous integration, followed immediately by a disintegration generating two (or more) new species. In other words, two species disappear, and two others take their places; the double decomposition being the result of two consecutive actions, and the heterogeneous disintegration following so closely on integration that it is difficult or impossible to arrest the change at the end of the first stage, so as to isolate the unstable species before it is destroyed. When these processes are confined within narrow limits of time and temperature,

the hitherto unexplained operation has been called catalysis, or action by presence.

§ 91. The generation, by homogeneous change, of species like the parents in centesimal composition we have designated metamorphosis. In homogeneous integration the identity of a species is lost in that of a new one of higher equivalent weight. In homogeneous disintegration this process is reversed, and a new species is formed, having the same centesimal composition but a lower equivalent weight. These two cases of metamorphosis correspond to what are called polymerization and depolymerization.

In many instances, as in the vapors of sulphur at different temperatures, and in pentene, and the various aldehydes and their polymers, the ratios between the equivalent weights of the species concerned are very simple; but in other cases, as in the polymers of many elemental species, such as carbon, tin, and phosphorus, in silicon dioxyd, and in native silicates and carbonates, these ratios are more complicated, and do not correspond to very simple fractions or multiples. Hence we infer, in the

process of metamorphosis, a temporary homogeneous disintegration of the species into more elemental forms, which, by redintegration, may give rise to new species, either of higher or of lower equivalent weights than the parent.

§ 92. Some species with difficulty assume or maintain a polymeric state,—as, for example, carbon dioxyd, which is liquid only at very low temperatures, or under great pressure, and, moreover, forms a very volatile and unstable solid; while other species, like carbon itself, silicon, and silicon dioxyd, are known to us only in dense polymeric forms, of great though different degrees of condensation. Between these two extremes are bodies which, like phosphorus, pentine, and the aldehydes, yield various polymers of different degrees of complexity and of stability.

All known liquid and solid species, whether elementary or not, are polymers of some simpler species, which, in very many cases, is capable of assuming the form of a gas or vapor. Such vapors themselves are sometimes polymers which, at higher temperatures, may be re-

solved into still simpler forms by homogeneous differentiation, as in the case of metaldehyde, of sulphur-vapor below 500° , and of iodine-vapor below 800° . Theoretically, we may suppose that even oxygen, nitrogen, and hydrogen may also undergo such resolutions at higher temperatures and under diminished pressure. There are, however, many solid species which, from the facility with which they undergo heterogeneous differentiation, or from their high equivalent weights, cannot exist in the vaporous state.

By integration, alike in metagenesis and metamorphosis, we rise to higher chemical species, and by disintegration descend to simpler ones. If, as we may suppose, all chemical species have come from one primal matter, it follows that the final disintegration of all so-called elementary species must be a homogeneous one, giving rise to that primal substance, which can only be conjectured to be a species much more attenuated than hydrogen, and possibly identical with the matter giving the green line 1474 of the corona, or some other unknown solar element.

§ 93. The condensation of gases into solids

or liquids, and the fusion and volatilization of these, when not attended with heterogeneous disintegration, are examples of metamorphosis. All such changes of state — the conversion of water into steam, the condensation of this again into water, its conversion into ice, and the fusion and evaporation of the latter — are, consequently, chemical processes. The precise nature of the liquid and of the colloid or porodic state, as compared with crystalline individualized solids, is not yet clear. The passage from the colloid to the crystalline, as well as that from the liquid to the crystalline, is generally attended with condensation ; while the fusion of a solid is a metamorphosis by expansion. To this, however, the conduct of water, and some other bodies in solidification, offers an exception. The same vaporous species, steam, gives rise by polymerization to the two distinct species, water and ice, having different equivalent weights. Analogies to this are seen in the different forms of liquid and solid phosphorus, and of tin, in the various liquid and solid species of di-pentines or turpentine-oils with different specific gravities and boiling-points, and in

the isomeric butylic alcohols, as well as in native silicates and carbonates. It is probable that the so-called isomers of other non-volatile bodies, like the different tartaric acids, are polymers similar in their constitution to these.

By polymerization, or homogeneous integration, the normal gaseous or volatile species are thus changed into liquids and solids of greater or less degrees of condensation. Of these the denser, other things being equal, are the harder and the more stable or indifferent to chemical changes such as fusion and solution. This relation has been illustrated at length by showing that the hardness and fixity of native sulphids, oxyds, carbonates, and silicates, and their resistance to the action of solvents, augment with the condensation of the species.

§ 94. All chemical changes are subordinated to measure and weight, as shown in the law of definite proportions alike by volume and by weight. The law of numbers is made evident, not only in multiple proportions, and in metamorphosis, but in homologous or progressive series, which, so far from being confined to certain hydrocarbonaceous species, are

found throughout all classes of chemical compounds.

In the combination or integration of gases and vapors the volumes uniting are lost in that of the product, there being an identification of volume. The converse is true in decomposition, or disintegration, which is differentiation. The fact that this law of volumes is universal, and applies not only to gases and vapors but to liquids and solids, has been obscured by the false assumption that the volume for solids is a variable and arbitrary quantity, conditioned by crystalline form; so that no constant comparison was possible between the volume of solids and that of gases. Moreover, there have hitherto been two distinct units of comparison, the one for gases, and the other for liquids and solids. The weight of a given volume of a gas or vapor as compared with that of the same volume of hydrogen gas at similar temperature and pressure, — which is its equivalent weight, — is, at the same time, its specific gravity, hydrogen being unity. The weight of a similar volume of a liquid or solid species is, on the contrary, compared with that of water;

and its equivalent weight varies as its specific gravity, that of water, which at its maximum density is the unit, being $1628 (\text{H}_2\text{O}) = 29,244$.

§ 95. In order to compare liquids and solids with gases and vapors, it is necessary to refer them to a common standard of density, or, in other words, to determine the relation of density between water and hydrogen gas. This is the relation of $d:p$ in the proportion $d:p::1:v$, provided d be the density of water at 4° , and p that of hydrogen at 0° . To fix this relation we compare the weights of a given volume (one litre) of hydrogen and of steam at 760 mm, and 100° , with the same volume of water at the same temperature; remembering, meanwhile, that this liquid at 4° has a weight of 1000 grams to the litre. We have thus the means of determining the specific gravity of hydrogen gas, of steam, and of water at 100° , — the temperature of its ebullition and its condensation at 760 mm., — as compared with water at its maximum density, which has been assumed as the unit of specific gravity for liquids and solids.

§ 96. With gases and vapors, the equivalent

weights of which are directly as their densities, it is evident that in the proportion $d : p : 1 : v$, we have $d = p$. But when this formula is applied to liquids and solids, while p still represents alike the equivalent weight and the density (hydrogen being unity) of the normal gaseous species, d is made to represent the density of some polymer thereof. In the case of water itself, where $p = 17.9633$, is both the equivalent weight and the density of steam, H_2O (hydrogen gas, $\text{H}_2 = 2.0000$), d represents the weight of that liquid at its maximum density (which is assumed as the unit of specific gravity). We have then :—

$$1.0000 : 17.9633 :: 1 : v = 17.9633.$$

The number thus found is the reciprocal of the coefficient of the condensation suffered by p in passing from the gaseous condition to the density in question. To determine the amount of this condensation we have simply to compare the weight of equal volumes of the gaseous p and the liquid d at the same temperature, or, in other words, knowing the weight of a litre of steam, H_2O , at the standard pressure, and 100° ,

to compare it with the weight of a litre of water at 100° . In this way we have found that water is formed by the condensation into one volume of 1628 volumes of H_2O , and consequently that $1628 \times 17.9633 = 29,244 =$ the equivalent weight of water; its specific gravity at 100° being 0.95878.

In the proportion $d:p::1:v$, as applied to any liquid or solid species, p does not represent its real equivalent weight, but the weight of the normal species which, by its condensation, gives rise to the liquid or solid. The value of v is thus that of the reciprocal of the coefficient of condensation. The equivalent weight of water (and of any other species having a specific gravity of 1.000) being as given above, we have $29,244 \div v =$ the coefficient of condensation.

From these data, remembering that the law of volumes is universal, and that equivalent weights are but the weights of equal volumes, it is clear that the equivalent weight varies directly as the specific gravity; so that, this being known, it is easy to calculate the true equivalent weight of any species.

§ 97. The phenomena of temperature, radiant energy, and electricity, apparent in chemical changes, do not belong to chemism, but to dynamics. To the dynamical history of species pertain all questions as to the atomic or molecular constitution of matter, on the one hand, or its infinite divisibility, on the other. Continued subdivisions cannot effect the destruction of a chemical species, which is an integer or unit, in which the existence, as such, of none of the species which may be obtained by its disintegration can be affirmed. No hypothesis as to an atomic or molecular structure, framed to explain dynamic phenomena in any given species, can, therefore, be legitimately extended to explain the generation of those species which may be derived from it either by integration or disintegration. For these reasons it is conceived that all such hypotheses, however useful they may be found in the explanation of certain dynamical phenomena, are foreign to the domain of chemistry, and should hold no place in the theory of the science.

§ 98. The chemical process is subordinated to the influences of pressure, temperature, and

radiant energy. Pressure influences chemical change, as seen in its relations to vaporization, and to heterogeneous dissociation, as well as to solution and to fusion; all of which it aids or restrains according as these are attended by condensation or expansion. A remarkable case is seen in its effect on the brittle species of tin, which, by pressure, undergoes a ready metamorphosis into the denser species. In like manner, as W. Spring has shown, ordinary phosphorus is, by great pressure, changed into one of the denser red species (§§ 5, 54). Heterogeneous integration is moreover directly effected thereby, as in Spring's experiments upon mixtures of metals with sulphur, or with each other.

Heat promotes union within certain limits, as seen in the solution of many substances in water, and in combustion; where, however, it may act by first causing dissociation, since nearly all species known are disintegrated at sufficiently high temperatures, when the tendency to integration is nullified, and matter becomes indifferent to chemical change. Heat is the universal disintegrator; and change of

state comes in the primal matter by reduction of temperature, and increase of pressure, with which chemical integration begins. Radiant energy also effects chemical change, as seen in the action of light; and the electric current causes chemical disintegration, in a way not yet well understood.

Chemism, however, is not to be confounded with any of the dynamic agencies just mentioned. It is one of the manifestations of an energy pertaining to matter, which inclines it to integration or disintegration, as conditions favor the one or the other mode of change. The energy thus displayed in change of state appears also in these dynamic activities, and is one and the same, whether manifested on the plane of dynamics, on that of chemism, or on the higher plane of biotics; but it is an error to confound either dynamical or biotical with chemical activity.

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CONTENTS. — PREFACE; I., Nature in Thought and Language; II., The Order of the Natural Sciences; III., Chemical and Geological Relations of the Atmosphere; IV., Celestial Chemistry from the Time of Newton; V., The Origin of Crystalline Rocks; VI., The Genetic History of Crystalline Rocks; VII., The Decay of Crystalline Rocks; VIII., A Natural System in Mineralogy, with a Classification of Silicates; IX., History of Pre-Cambrian Rocks; X., The Geological History of Serpentine, with Studies of Pre-Cambrian Rocks; XI., The Taconic Question in Geology; Appendix; and Index.

IN PREPARATION:

MINERALOGY ACCORDING TO A NATURAL SYSTEM.—The significance of the physical characters on which the Natural-History system of Mineralogy has been based, and their relations to the chemical characters of the system of Berzelius and his followers, are set forth in the author's volume entitled *A NEW BASIS FOR CHEMISTRY*, and more fully in his *MINERAL PHYSIOLOGY AND PHYSIOGRAPHY*, pages 279-401, 687, 688, where a tabular view of the Classes and Orders of the *NATURAL SYSTEM* is given, on page 382.

The principal points in the new treatise will be: (1) Arrangement of all native and artificial species of the mineral kingdom in classes and orders upon a chemical basis; (2) Their complex chemical structure and high equivalent weights; (3) Application to them of the principles of polymerism and of homologous or progressive series; (4) Direct relations of the constitution of solids, not only to their specific gravity, but to their hardness and their greater or less chemical indifference, which latter are shown to be connected with the variations in condensation or so-called atomic volume; (5) Recognition of the wide distinction between crystalloid and colloid or amorphous species; (6) Sub-division, on the above grounds, of the orders and sub-orders into tribes, which generally correspond with the orders of the Natural-History system; (7) Arrangement of tribes in genera and species, and designation of these by a binomial Latin nomenclature; (8) Systematic descriptions of native and of some related artificial species; (9) Genetic history of native species, and their artificial production; (10) Their relations to the great groups of rocks in the earth's crust.

